Inherent Safety Intervention Framework

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UNVIERSITI TEKNOLOGI PETRONAS

Inherent Safety Intervention Framework

By

©Ir. Chan Tuck Leong

A THESIS

SUBMITTED TO THE POSTGRADUATE STUDIES PROGRAM

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DEGREE OF

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I hereby declare that the thesis is based on my original work except for quotations and citations, which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UTP or other institutions.

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Date : 28 March 2008

Dedicated to

My ever loving wife, Sew Ping

Baby Chloe

&

My greatest supporters – mum & dad

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ABSTRACT

Despite being an attractive proposition in terms of safety and cost performance, the actual implementation of Inherent Safety in design is not widely observed in the industries. This has been documented in publications which indicated the lack of an effective Inherent Safety Quantification methodology and the lack of integration between process design stages with risk and consequence estimation are hurdles to designing inherently safer process plants.

Initial attempts by other researches to quantify level of inherent safety resulted in the invention of few indices which are based on reactions involved and have been able to differentiate the level of inherent safety for various routes producing the same product. These indices account for temperature, pressure and presences of the chemicals in the reactions individually. These indices are not able to reflect the interaction of these process parameters and the actual composition of the process streams and their impact on level of inherent safety.

This research developed a methodology which is able to differentiate level of inherent safety for various process routes and subsequently of the various process streams within a process route. The new indices known as Process Route Index (PRI) and Process Stream Index (PSI) are based on interactions of various process parameters and actual composition of process streams. These indices are part of the Inherent Safety Intervention Framework (ISIF) which is proposed and proven in this research to allow for proactive identification of consequences of a hazard and subsequently allow modifications based on Inherent Safety principles. Owing to its integration with process simulator, the ISIF can quickly reflect the changes of inherent safety levels when process modifications are simulated iteratively.

In order to represent risk in a format familiar to many, this research proposed the concept of Inherent Risk Assessment (IRA) which is similar to Quantitative Risk Assessment (QRA) which is widely used. Similar to QRA, the IRA represent risk by means of a FN Curve. IRA reflects the inherent risk within the process being designed without yet considering mechanism and procedures to reduce risk to an ALARP level as the design stages progresses along. It is proposed that the IRA be used to determine

initial acceptance, by government agencies, of a process being designed based on predetermined set of assumptions.

The case studies presented towards the end of this research clearly demonstrated the effectiveness of the ISIF to quantify level of inherent safety at process route selection level using PRI and using the PSI to prioritize streams for modification purposes. Based on the PRI, an inherently safer route can be chosen and modification based on the principles of inherent safety can be implemented at the streams scoring higher PSI numbers. The IRA complements the work by representing the level of risk inherent to the process being considered in comparison to the limits set by local authorities.

ABSTRAK

Walaupun konsep "Inherent Safety" didapati boleh mendatangkan manfaat dari segi keselamatan dan kos, ianya belum mendapat sambutan baik dari pihak industri. Keadaan ini telah tercatat dalam beberapa kajian terdahulu yang berpendapat bahawa keadaan ini disebabkan oleh kekurangan kaedah-kaedah "Inherent Safety Quantification" serta ketiadaan integrasi antara langkah-langkah rekabentuk proses dan kaedah menjangka risiko dan akibat.

Dalam usaha-usaha awal untuk mengukur tahap "Inherent Safety" bagi pelbagai rekabentuk, para pengkaji telah mencipta beberapa indeks yang berasaskan tindakbalas yang terlibat. Indek-indek awal ini boleh mewakili suhu, tekanan dan kehadiran bahan-bahan kimia secara individu. Akan tetapi, indek-indek ini tidak berupaya mewakili keadaan sebenar dalam sesuatu proses kerana indek-indek awalan ini tidak mengambilkira interaksi di antara parameter-parameter proses dengan komposisi bahan-bahan kimia.

Kajian ini mencipta satu kaedah baru yang boleh membezakan tahap "Inherent Safety" bagi pelbagai laluan-laluan proses dan seterusnya bagi setiap aliran dalam sesuatu proses yang tertentu. Indek-indek rekaan baru ini dikenali sebagai "Process Route Index (PRI)" dan "Process Stream Index (PSI)". Indek-indek ini adalah berdasarkan interaksi semasa parameter proses dan komposisi dalam aliran tersebut. PRI dan PSI adalah sebahagian daripada "Inherent Safety Intervention Framework (ISIF)" yang dikemukakan dan dicipta dalam kajian ini. Oleh kerana ISIF digabungkan dengan perisian simulasi proses, ia didapati boleh mengenalpasti kesan-kesan bahaya dan membolehkan pengubahsuaian tertentu mengikut prinsip "Inherent Safety" untuk menghasilkan proses yang lebih baik dari segi "Inherent Safety".

Kajian telah mencadangkan konsep "Inherent Risk Assessment (IRA)" yang mirip dengan "Quantitative Risk Assessment (QRA)" untuk mewakilkan tahap risiko dalam bentuk yang dikenali ramai. IRA mewakilkan tahap risiko melalui "FN-Curve". IRA mewakili risiko intrinsik sesuatu proses yang sedang direkabentuk tanpa mengambil kira langakah-langkah pengurangan risiko yang bakal ditambah apabila rekabentuk menjadi lebih mantap. Adalah dicadangkan bahawa IRA digunakan untuk

mendapatkan kebenaran awal dari agensi kerajaan untuk proses yang sedang direkabentuk berdasarkan anggapan-anggapan tertentu.

Kes-kes yang dibincangkan di penghujungan kajian ini membuktikan keberkesanan ISIF untuk mengukur tahap "inherent safety" pada peringkat pemilihan laluan proses melalui PRI manakala PSI digunakan untuk menyusun aliran-aliran dalam sesuatu proses mengikutan keutamaan untuk pengubahsuaian. PRI boleh digunakan untuk mengenal pasti laluan proses yang secara intrinsiknya lebih selamat dan pengubahsuaian mengikut prinsip-prinsip "Inherent Safety" boleh ditujukan kepada aliran-aliran yang mempunyai indek PSI yang tinggi. IRA pula melengkapkan ISIF dengan memberi perwakilan tahap risiko intrinsik sesuatu proses untuk perbandingan dengan had yang ditetapkan oleh agensi tempatan.

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CHAPTER 1

Introduction

1.0 INTRODUCTION

Health, Safety and Environment (HSE) is the utmost important aspect in the operations of petrochemical, 0il and gas industries in order to produce desired product without interruption. These plants are typically engineered by following a sequence of design stages, which may defer from project to project due to varying process complexity and individual company's internal standards. In 1989, the Center for Chemical Process Safety (CCPS) of the American Institute of Chemical Engineers (AIChE) published the typical phases of a capital project, shown in Figure 1.1, which includes conceptual engineering, basic engineering, detail engineering and subsequently procurement, construction and commissioning of the facilities.

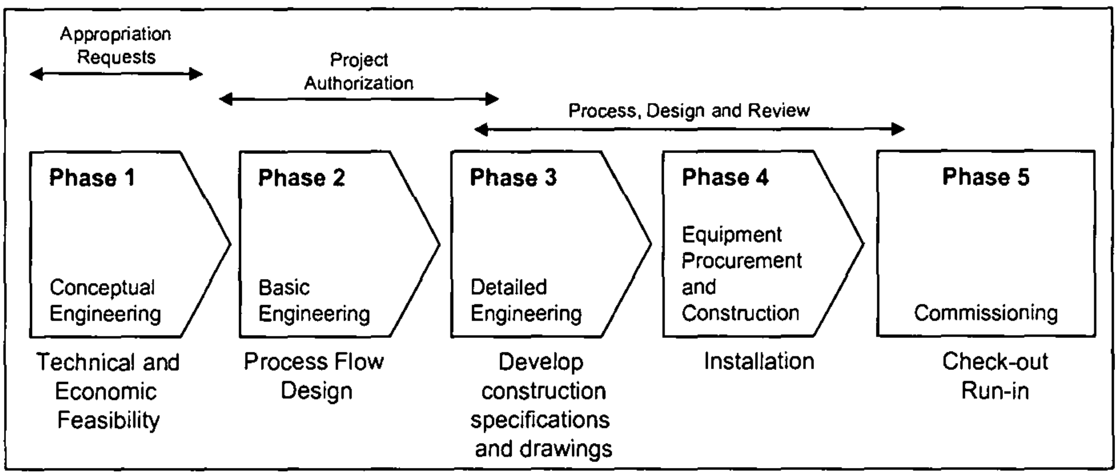


Figure 1.1 : Phases of a capital project (CCPS, 1989)

Figure 1.2 shows the typical project phases expanded from Figure 1.1 to cater for specific project requirements within Petrochemical, Oil and Gas Industry along with the expected cost estimation and HSE considerations. Safety is considered in concurrent and often towards the end of process design. Safety analysis like Quantitative Risk Assessment (QRA) is also not formally integrated with the design.

All these phases as shown in Figure 1.1 and Figure 1.2 involve expertise from various engineering disciplines e.g. mechanical, chemical, electrical etc. The interaction of these engineering disciplines is illustrated in Figure 1.3. Chemical or process engineering often plays key role in the initial or conceptual design phase which determines the process routes and main process parameters. The accuracy of input from process engineering determines the outcome of the design including safety and environmental performance.

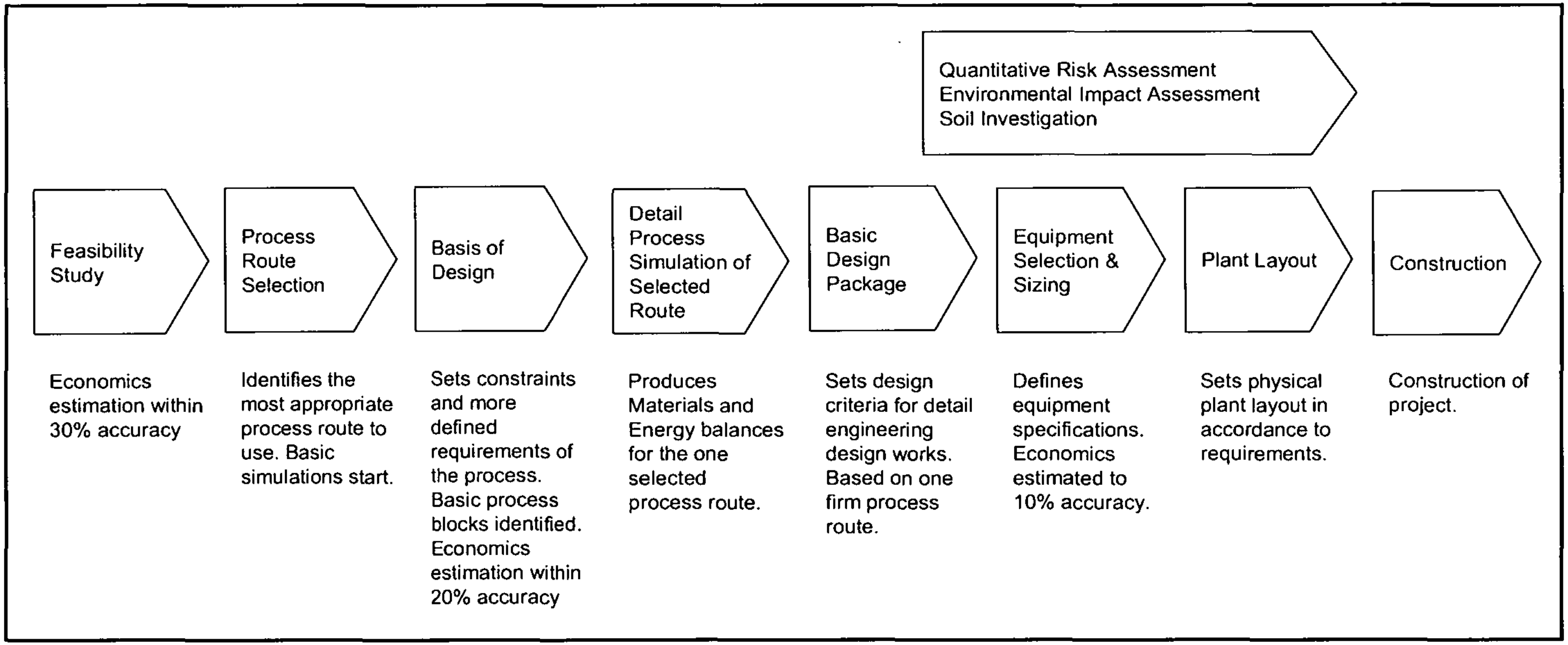


Figure 1.2 : Typical plant design stages in oil and gas industries

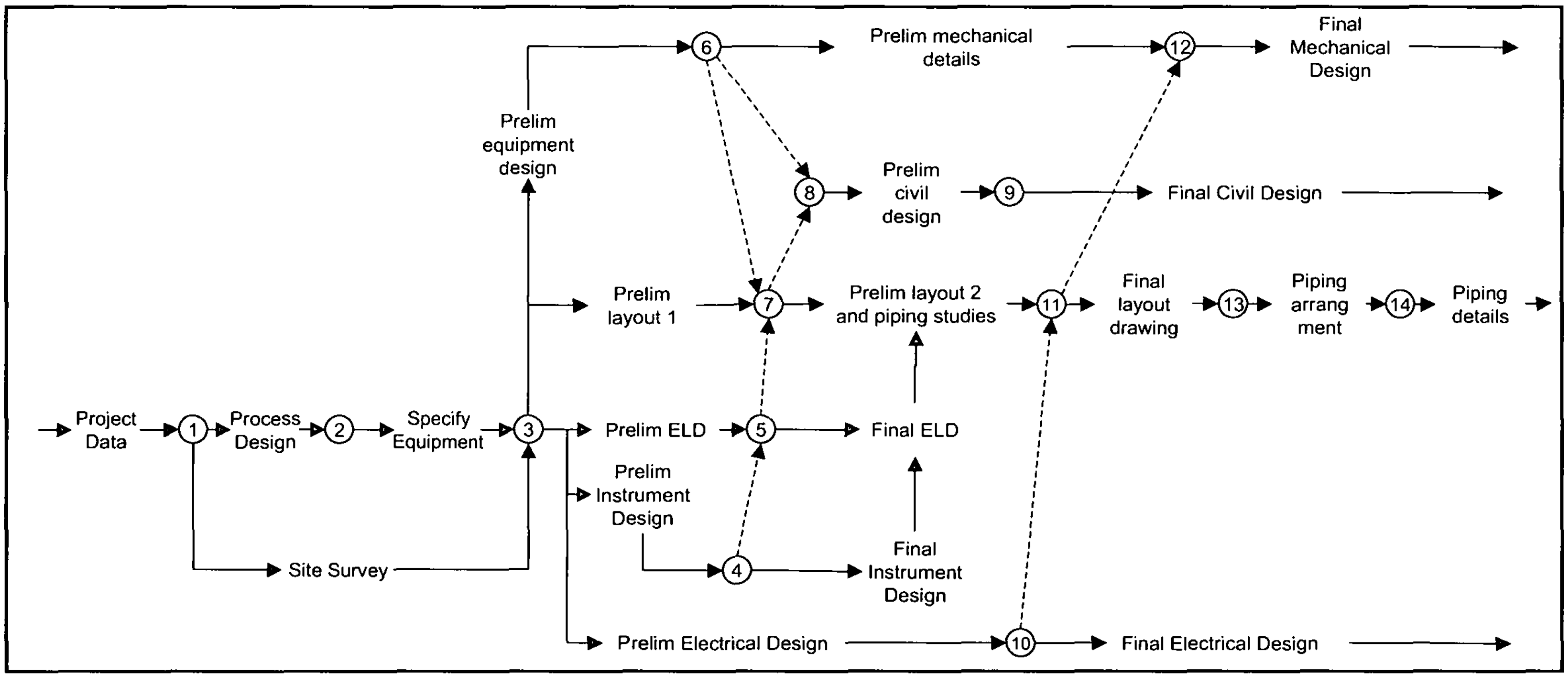


Figure 1.3 : Typical plant layout and design network (Mecklenburgh, 1985

Over the past few decades, conceptual process design for chemical process industries had changed and improved tremendously. Siirola (1996) of Eastman Chemicals Company, Kaibel (2002) of BASF and Harmsen (2004) of Shell Research and Technology, provided a general picture of all lifecycle steps of industrial projects and the related process engineering deliverables, which are being compiled in Table 1.1.

Table 1.1 : Chemical process plant lifecycle and process engineering deliverables

Life cycle step	**Process Engineering Key Deliverables**
Chemical route synthesis	▪ Development of chemical synthesis steps ▪ Selection of best chemical synthesis steps
Conceptual process design	▪ Function integration ▪ Heuristic selecting unit operations and recycle structure ▪ Superstructure optimization
Process development	▪ Experiments for kinetic, physical data ▪ Reaction and separation tests ▪ Pilot plant ▪ Cold flow scale-up tests
Process engineering	▪ Definition of all equipment and control for accurate economic evaluation
Site integration	▪ Connect energy and mass flows with other processes and utilities
Detailed engineering	▪ Definition of all process details to allow purchasing and construction
Plant operations	▪ Production phase
End of life	▪ Find second use ▪ Deconstruct and reuse parts

The above design stages are applicable to commonly known processes in which, much of the data pertaining to properties and characteristics are available. However, when there is a requirement to use and design novel technologies, additional efforts must be to put in to ensure safety and profitability. The development efforts for a novel industrial process are compiled from descriptions by Siirola (1996) of Eastman Chemicals Company Kaibel (2002) of BASF and Harmsen (2004) of Shell Research and Technology. These steps are in addition to those given in Table 1.1.

1. Make a first scouting conceptual design.
2. Determine the physical and chemical properties, crude kinetics and critical construction material choice parameters required for the design, and some proof of principle experiments.
3. Make a conceptual design for the commercial scale plant and a pilot plant.
4. Operate the pilot plant.
5. Design the commercial plant based on the pilot plant findings.

1.1 Safety In Conceptual Design Stages and Plant Lifecycle

Safety aspects of process plants have been given high priority, and have been further intensified after the Flixborough and the Bhopal incidents. Many guidelines and procedures have been developed, especially over the last three decades, with respect to safety of chemical process plants, which often include gas plants, petrochemical plants, refineries etc., by the industries themselves, for instance HAZOP by ICI, DOW Fire and Explosion Index by DOW Chemicals. The CCPS (1993) of the American Institute of Chemical Engineers (AIChE) has identified a number of hazard analyses techniques and methodologies, which are deemed suitable for respective plant design stages. The recommendations are shown in Figure 1.4. More in depth reviews of traditional safety methodologies are provided in Section 2.1.

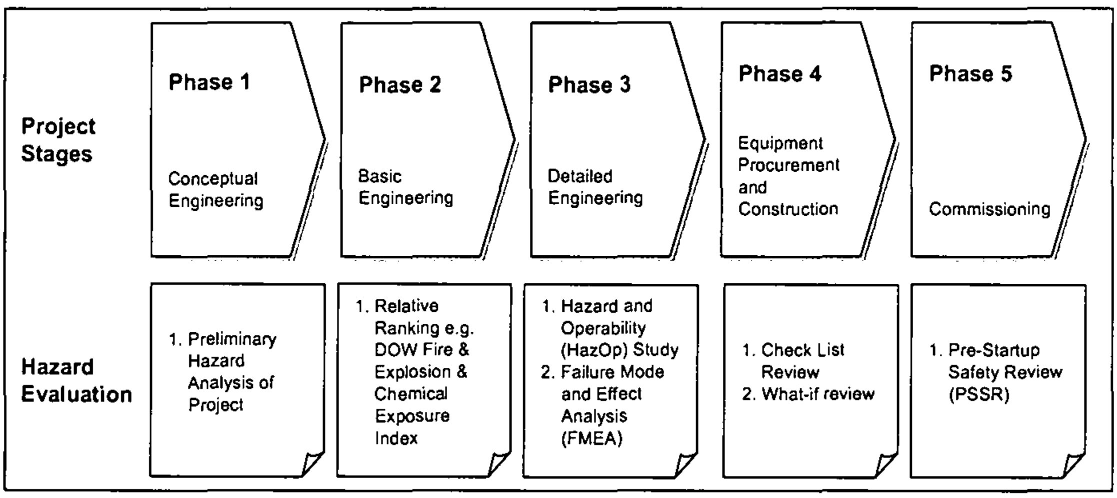


Figure 1.4 : Hazard evaluation at various project stages (CCPS, 1993)

Taylor (1994) puts the safety program shown in Figure 1.5 to include the Operations phase, which not only involve technical reviews issues but also include training of the operators and maintenance crew who will be operating and maintaining the plant. It also covers safety analyses in the course of construction.

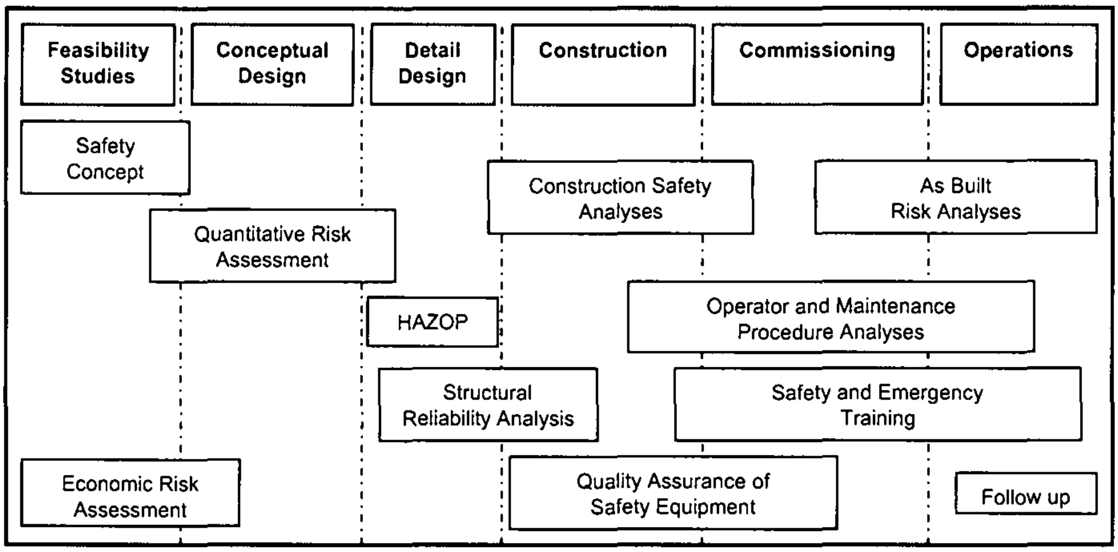


Figure 1.5 : A full program of safety analysis (Taylor, 1994)

Techniques described in Figure 1.4 and Figure 1.5 are often applied in parallel to chemical process plant design stage and not as an integral part of the design process. Design information are of the manually transferred into safety analysis software which in turn will provide indication of potential hazards and the related risks. When potential risks are detected, more often than not, consequence minimization or mitigation measures and/or equipment are put in place. However the safety devices not only require additional maintenance (hence cost) but are also susceptible to unrevealed failures. Unrevealed failures of protective device will result in the plant experiencing same risk as before.

Over the last decade, Quantitative Risk Assessment (QRA) has gained a wide acceptance as powerful tool to identify and assess the significant sources of risk and evaluate alternative risk control measures in chemical process industries. QRA is a highly structured study which documents the best knowledge of the company's technical experts on the potential risks. Application of QRA has contributed to not only increased safety but also improved cost effectiveness in many areas (Shell International Exploration and Production B.V, 1995). Methodology to perform QRA outlined by Shell can be found in Figure 2.5.

Other equally important factors to ensure successful implementation of safety features are human error and ethics. M. Papadaki (2007) deliberated that softer issues of human behavior, ethics and human errors very often than not, are the contributing factors for defeated safety protection functions. She argues that constant education for better ethics and human behavior is required to improve inherent safety in daily lives along with appropriate hardware and system designs.

1.1.1 Inherent Safety Concept And Implementation Challenges

Since the passive safety techniques as described above are not able to proactively reduce or eliminate the source of risk, a new approach known as Inherent Safety was formalized in the early 90's by Kletz. Inherent Safety is based on proactive identification and subsequently addressing the potential hazards and resulting risks. These principles are further elaborated in Section 2.6. Even though the principles of Inherent Safety are appealing to many, they have not been widely applied in the industry due to several factors. Many researchers including Harstad (1991), Kletz (1991), Mansfield, Kletz, and Al-Hassan, (1996), Rushton et al. (1994), Moore A.D. (1999), Khan and Amyotte (2002); identify the lack of proper tool and system for its implementation as a key factor to poor application in the industry.

The other factor is the lack of methodology to quantify the inherent safety level (ISL) of designs during initial design stages, which is essential in the decision making process driving implementation of Inherent Safety Designs. In order to address the problems relating to quantification of ISL, Lawrence, (1996); Heikkilä, (1999); Palaniappan, (2002); Gupta and Edwards, (2003); Khan and Amyotte, (2004); pioneered the development of inherent safety indices. Each method has its own advantages and drawbacks in actual applications. Critical review of each index is provided in Section 2.7 of this thesis.

1.1.2 Computer Tools For Risk Assessment and Process Design

Few major software used in risk assessment include Software for the Assessment of Flammable, Explosive and Toxic Impact (SAFETI), Process Hazard Assessment Software Tool (PHAST) from Det Norske Veritas (DNV) and Fire, Release and Dispersion (FRED) from Shell. Reviews of the software will be further discussed in Section 2.5.

SimSci and ASPENTECH have developed and perfected process simulation suites like, Pro/II, HYSYS (renamed as UNISIM upon takeover by Honeywell in year 2005) and ASPEN+ to simplify process calculations. Using such tools, design engineers would be able to quickly calculate response of the entire process to changes in parameters like pressure, temperature or composition. Information from the software is then used in process equipment design, resulting in better and robust designs.

The program architectures ensure the process simulator can create, manipulate, and evaluate cases rapidly and effectively. These simulators play important roles to provide fast and efficient platform to optimize process conditions and solve highly technical process problems. Sophisticated solving techniques ensure cases are robust and can be worked quickly.

Recent developments in process simulation technology, for example UNISIM, resulted in more integration to allow users to even perform online optimization, performance monitoring and business planning (Honeywell, 2007).

To address safety concerns effectively from design stages, process simulators should have the capabilities to assess risk levels resulting from specified process conditions. However, current process simulators are not equipped with tool to determine risks and effects related to the operating conditions and present consequence analysis software are able to study the sensitivity of varying process conditions to risk.

By taking advantage of Object Linking and Embedding (OLE) automation technology, HYSYS users have the ability to combine the capabilities of HYSYS with other third party, for instance Microsoft application or in-house applications. The HYSYS architecture allows additional accessibility beyond the interface, including easy programming of the details of streams and operations, as well as case manipulation such as changing flow sheet topology. The end users do not need to see the HYSYS source code or even understand what was required to expose the objects. All that is required is the knowledge of those objects that are available (Hyprotech, 1999).

1.2 Explosions In Chemical Process Industries

An explosion is defined as a process whereby a pressure wave is generated in air by a rapid release of energy (Major Hazards Assessment Panel, 1994). Explosions can be classified as detonation or deflagration, depending on speed of the accelerating flame fronts. If flame front moves at or above speed of sound then the explosion is assumed as detonation otherwise it is a deflagration. Detail discussions of explosions are presented in Chapter 3.0.

Historical records show that monetary losses as well as loss of lives associated with hazards in process industries are substantial. According to a survey by J&H Marsh & McLennan Consulting (2001) shown in Figure 1.6, explosions and vapor cloud explosion cause the highest average damage per incident (average million dollar loss) in 100 large property damages in hydrocarbon processing industry due to various hazards from 1970 to 1999. Since the vapor cloud explosions result in largest damage, this present research uses it to demonstrate consequences of release of materials from process plants.

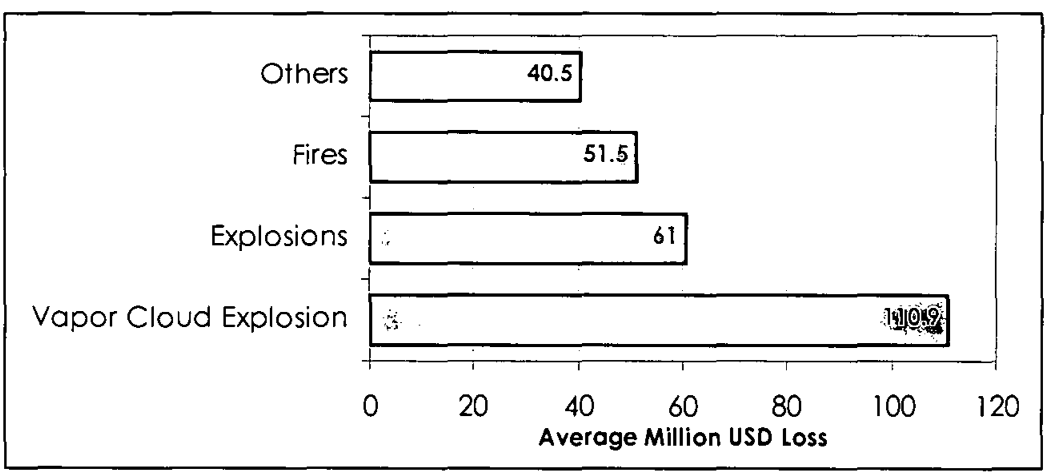


Figure 1.6 : Average dollar loss to types of major hazards in hydrocarbon industries, (J&H Marsh & McLennan Consulting, 2001)

In terms of event frequencies, Figure 1.7 shows that explosion forms the highest percentage of events in gas plants and petrochemical plants. Explosion event is the second highest event in refineries; possibly due to nature of processes being mainly liquid based which is less volatile compared to gases. On average, explosion made up 55% of the events, fire incidents made up 31%, mechanical failure made up 8% while the events due to other causes made up the remaining percentages.

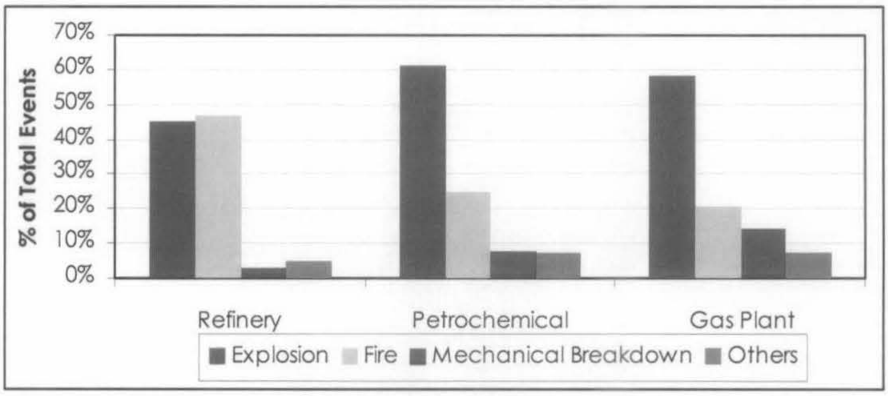


Figure 1.7 : Type of incidents in various plants for 30 years, (J&H Marsh & McLennan Consulting, 2001)

In a recent report (Shell Global Solutions International, 2005), normal operations or steady state operations phase is when most of the fire and explosion incidents occur. This is represented in Figure 1.8. From this figure, it can be inferred that risk reduction efforts should be focused on operations phase (steady state) since approximately 60% of fire and explosion incidents happened during this phase.

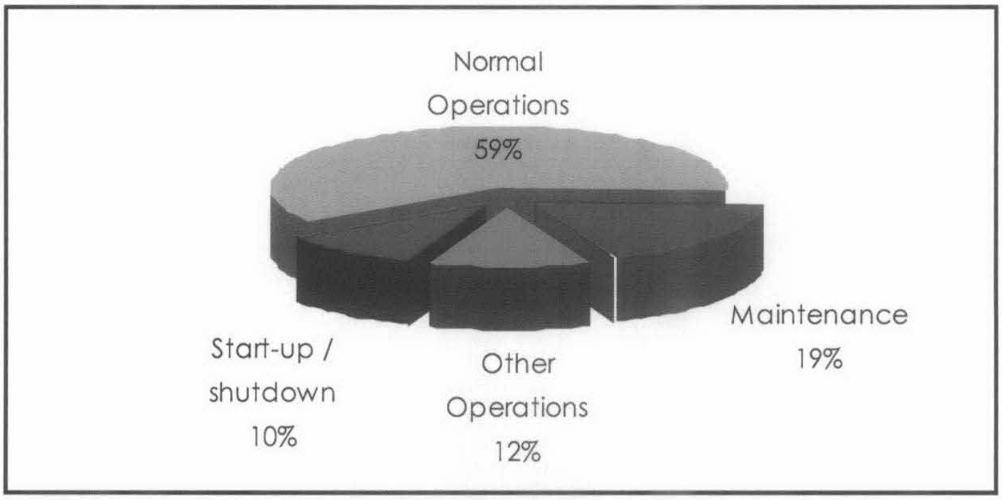


Figure 1.8 : Phases of operations in which fire and explosion events occur (Shell Global Solutions International, 2005)

1.3 Problem statement

Many safety management techniques have been developed and used over the years to address safety aspects of chemical processes. However, many of these techniques, shown in Figure 1.4 and Figure 1.5 and those described in Section 2.1 are used in series and usually towards the end of detail process design stages. For instance, QRA, being the most popular choice is often carried out after the process design has been completed. This can be attributed to the fact that present software for design is not capable of performing even the simplest risk assessment.

While recent developments in safety research call for implementation Inherent Safety in designs, the lack of systematic methodology and technology is hindering its adoption in large scale. Quantification of Inherent Safety Levels (ISL) of each design option presents further challenge.

The present research addresses these two shortcomings by proposing a framework (Chapter 4.0) for Inherent Safety Intervention Framework (ISIF) during initial process design using process simulator. ISIF adopts the structured approach of QRA at the early phases of simulation thus allowing proactive risk control and reduction measures to be implemented in accordance to principles of Inherent Safety. The research also proposes a two tier Inherent Safety Index to quantify ISL at process route selection level and subsequently at process streams levels. The new indices (Section 4.1) which address shortcoming of current indices are also derived by considering interaction of process parameters and process streams as resulting mixture rather than pure components.

1.4 Research Objectives

This research hypothesizes that inherently safer processes can be designed by integrating an index based screening tool, providing effective means of evaluating risk and consequences into the process design stages. The research endeavors to address the following objectives:

i. To develop a framework to assess inherent risk during preliminary design stage by integrating the process design simulator with inherent safety index, risk and consequence analyses. The framework utilizes the principles of Inherent Safety in order to produce inherently safer design.
ii. To devise a two-tiered inherent safety index system for overall process and stream level assessments based on parameters of flammable materials in order to quantify explosion risk factors
iii. To translate the above framework and index system into a workable software tool for integration with process simulator
iv. To validate the tool using established data and case studies
v. To conduct case studies using the developed tool in order to justify the potential application of inherent risk assessment to produce inherently safer designs

1.5 Research Scope

The present research is guided with the following scopes to ensure the research addresses the objectives and is completed within stipulated time frame.

i. The research is limited to designing a prototype to demonstrate the application of the proposed framework in the context of Vapor Cloud Explosion (VCE) as this hazard causes the largest amount of monetary losses and resulted in highest number of casualties.

ii. In order to model consequences of VCE, the present work used TNO Correlation Method and the Sach Overpressure Equations as these equations and correlations are widely acceptable by industries and government agencies.

iii. The research focused on studying leaks from process streams under steady state conditions. Releases are modeled leaks from pipes. Depending on flow characteristics the leak is sub-classified as choked or non-choked flows. All releases are assumed to be in vapor form. The research does not consider transition of choked flow regime to non-choked regime, as it is a function of time, which is not available in steady state simulation.

iv. Microsoft EXCEL and Visual Basic for Applications (VBA) are used as development platforms for the risks and consequence estimation tool while HYSYS simulator is used as process simulation platform.

CHAPTER 2

Literature Review

2.0 LITERATURE REVIEW

Major accidents in chemical industry have occurred worldwide especially with the industrialization after the Second World War. In Europe, in the 1970's two major accidents in particular prompted the adoption of legislation aimed at the prevention and control of such accidents. The Flixborough accident in the United Kingdom in 1974 was a particularly spectacular example. A huge explosion and fire resulted in 28 fatalities, personnel injury both on and off-site, and the complete destruction of the industrial site. It also had a domino effect on other industrial activities in the area, causing the loss of coolant at a nearby steel works, which could have led to a further serious accident.

The Seveso accident happened in 1976 at a chemical plant manufacturing pesticides and herbicides. A dense vapor cloud containing tetrachlorodibenzoparadioxin (TCDD) was released from a reactor, used for the production of trichlorofenol. Commonly known as dioxin, this was a poisonous and carcinogenic by-product of an uncontrolled exothermic reaction. More than 600 people had to be evacuated from their homes and as many as 2000 were treated for dioxin poisoning.

Another notable accident was at the Union Carbide factory at Bhopal, India (1984) where a leak of methyl isocyanate caused more than 2500 deaths.

On 25 September 1998, the Esso gas processing and crude oil stabilization plant at Longford, Victoria, Australia, suffered a hydrocarbon release that ignited, causing 2 fatalities and 8 injuries, and led to a series of escalating fires and explosions. The plant was shut down, causing massive disruption to gas supplies throughout Victoria for 2 weeks (Spouge, J.R. and Pitblado, R.M., 2000)

Another recent major incident is the BP Texas City Refinery explosion which is one of the worst industrial disasters in recent U.S. history (U.S. Chemical Safety And Hazard Investigation Board, 2007). On March 23, 2005, at 1:20 p.m., the BP Texas City Refinery suffered Explosions and fires which killed 15 people and injured another 180, alarmed the community, and resulted in financial losses exceeding $1.5 billion. The incident occurred during the startup of an isomerization unit when a raffinate splitter tower was overfilled; pressure relief devices opened, resulting in a flammable liquid geyser from a blow down stack that was not equipped with a flare. The release of flammables led to an explosion and fire. All of the fatalities occurred in or near office trailers located close to the blowdown drum. A shelter-in-place order was issued that required 43,000 people to remain indoors. Houses were damaged as far away as three-quarters of a mile from the refinery. Up to present time, investigators are still unable to conclude on the actual mechanism that occurred during that time, but retrospective modeling works by Khan and Amyotte (2007) indicated the venting on hydrocarbon could have prevented a more devastating incident.

These are some examples of major incidents, which had further amplified the seriousness of safety in the process industries. Figure 1.6 has illustrated the monetary losses resulting from such unfortunate incidents. From the same figure, it can also be concluded explosions caused the greatest damage. At such, safety concerns resulting from potential risks especially explosions should be considered and addressed in the whole lifecycle of a process system or a facility (Greenberg and Cramer, 1991). Taylor (1994) illustrates this opinion in Figure 1.5, which shows that safety and hazard analyses need to be carried out throughout the lifecycle of a process plant from the beginning i.e. feasibility study right till the operations phase. Some of the techniques are further discussed in Section 2.1.

Presumably all the process plants described above had one way or another undergone such scrutiny at the time of the design and construction and yet such catastrophic incidents occur. This has brought about the introduction of the Inherent Safety Principles formalized by Kletz in the early nineties. These catastrophic events, when studied retrospectively, could have been avoided or at least their impact minimized if Inherent Safety Principles had been applied to the designs. Sanders (2003) reviewed several cases including the Flixborough incident, and concluded that "Exercising the principles of inherent safety would have reduced the severity and perhaps the opportunity of these events". Khan (2007) further supported this view by demonstrating the applications of several Inherent Safety Principles which are deemed to be able to reduce the impact from the Bhopal and Piper Alpha incidents.

Noting the importance and potential of proactively designing out potential hazards and hence risk, the present research work aims to derive a mechanism to assist the quantification of the different level of safety of various design and thus allowing implementation of the Inherent Safety Principles early in the design stages. This research uses explosion hazard to demonstrate the proposed concepts.

2.1 Hazard Analysis In Process Plant Lifecycle

The Health and Safety Executive UK (2001) defines hazard as the potential for harm arising from an intrinsic property or disposition of something to cause detriment while CCPS (1999) defines hazard as a chemical or physical condition that has the potential for causing damage to people, property or the environment.

Currently there are more than 62 methodologies developed to undertake hazard analysis (Tixier et. al., 2002) that may potentially result from a process plant that is being designed. Generally, the analyses become more detail and more complete as the projects matures and moves into operational stage, where most of the information is readily available. Applications of these techniques are driven largely by the available information at each design stage and the different types of results expected. For this research work, a number of commonly used techniques (Table 2.1) are reviewed.

Table 2.1 : Hazard analysis methodologies commonly used in industrial sites

a. DOW Fire and Explosion Index (DOW FEI)	b. Hazard and Operability Studies (HAZOP)
c. Fault Tree Analysis (FTA)	d. Event Tree Analysis (ETA)
e. Failure Modes and Effects Analysis (FMEA) and Failure Modes, Effects and Criticality Analysis (FMECA)	f. Relative Ranking

2.1.1 DOW Fire and Explosion Index (DOW FEI)

The DOW FEI is a rigorous hazard identification methodology developed by DOW Chemical Company back in 1964 and was later shared with the industry. It is one of the most popular methods of hazard survey (Crowl and Louvar, 1990). The DOW FEI is a systematic approach to identify hazards in chemical plant by following a structured rating form. The system is designed for rating the relative hazards from storage, handling and processing of explosive and flammable materials, free from individual judgment factors.

The DOW FEI method starts by identifying and dividing the process into separate process units. Since it is not practical to evaluate all units, a representative unit operation within the processes is selected. The material factor (MF) is selected from a predefined table. Generally materials (chemicals) of higher explositivity and flammability properties are accorded larger number. The hazards arising from process conditions are characterized in two factors i.e. the General Process Hazard Factor (F_1) and the Special Process Hazard Factor (F_2). Multiplication of these factors with material factor (MF) gives the Fire and Explosion Index (F&EI) shown as Equation 2-1. Table 2.2 shows the interpretation of the DOW Fire and Explosion Index (F&EI).

$$F\ \&\ EI = F_1 \times F_2 \times MF \qquad \text{Equation 2-1}$$

Table 2.2 : Degree of hazard and DOW Fire and Explosion Index

DOW F&EI	Degree of hazard
1 – 60	Light
61 – 96	Moderate
97 – 127	Intermediate
128 – 158	Heavy
159 and above	Severe

The expansion of this technique provides further detail analyses including estimation of Maximum Probable Property Damage (MPPD). The base MPPD is derived by estimating value of area of exposure multiplied with damage factor (provided as correlation in this method). The corrected MPPD is obtained by multiplying the based MPPD with a credit factor. The credit factor (C) gives credit to features of the plant that provide safety and protection. The credit factor (C) is the multiplication result of the Process Control (C_1), Material Isolation (C_2) and Fire Protection (C_3) factors. This technique provides a quantitative output of hazard analysis, which can be ranked.

This methodology has been further improved by subsequent researches, for instance, modification to calculation methods to reflect effects of various loss control measures (J.P. Gupta, G. Khemani and M.S. Mannan, 2003). An earlier paper by Gupta (1997) suggested some enhancements in several penalty values to account for conditions in developing countries.

C.B. Etowa et. al. (2002) attempted to relate the DOW FEI and CEI to various parameters that reflect inherent safety in process design. Their work, which is based on the MIC release in Bhopal incident, shows that FEI and CEI correlate to inventory, pressure and temperature. FEI and CEI are found to be proportional to increase of inventory and pressure and inversely proportional to temperature.

2.1.2 Hazard and Operability Studies (HAZOP)

The HAZOP was introduced by Imperial Chemical Industries (ICI) for review of chemical process design, which is then extended into other processes over the decades. Fundamentally the method assumes that system is safe when all operating parameters are at acceptable levels. The methodology systematically searches for hazards in the form of deviations from norm with dangerous consequences. Typically the parameters studied will include basic process conditions like temperature, pressure and flow. The study team follows a set of predefined guidewords to analyze possible deviation from normal conditions.

The HAZOP team undertakes a thorough examination of the process flow diagrams (PFD) and piping and instrumentation diagrams (PID) to identify deviations. It also allows for the team to evaluate consequences of operator errors.

The studies are carried out in a team and hence the quality of the study is highly dependent on the experience and open to influence of team members. The other disadvantage of this method is the required time and resources to conduct a study. The advantages of HAZOP include; pooling of expertise, its applicability to most of the process industries and is systematic.

HAZOP produces qualitative outputs often in a list of action items that need to be resolved to ensure safety concerns are addressed adequately. However, this approach provides little information on risks and consequences. As a result, this approach tends to "goldplate" a process design, resulting in large number of hazards being identified. Many of the hazards may have low probability or consequences (Crowl D.A., Louvar J.F., 1990).

2.1.3 Fault Tree Analysis (FTA)

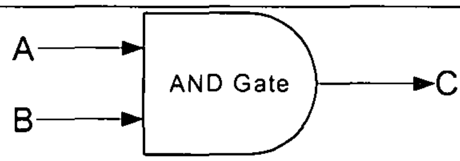
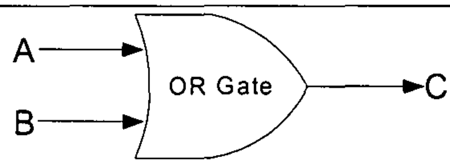
Fault tree analysis (FTA) explicitly expresses how equipment failures, operator errors, and external factors lead to system failures. As a powerful tool for risk assessment, FTA has long been successfully applied in the nuclear industry to predict the likelihood of hazardous incidents, identify major risk contributors, and quantify the benefits associated with safeguards (Wang, 2003). The FTA breaks down an accident hazard into contributing factors to investigate combination of events and conditions that lead to the hazard. The events and conditions can be evaluated in both quantitative and qualitative terms (Ireson et. al., 1995). The probability data that provide quantitative outputs can often be read from failure rates databank. FTA is a logical representation of events in graphical method of describing the combinations of events leading to a defined system failure. In the fault tree terminology the system failure mode is known as the top event.

The FTA involves essentially three logical possibilities and hence two main symbols. These involve gates such that the inputs below fates represent failures. Outputs (at the top) of the gates represent a propagation of failure depending on the nature of the gate. The three types are:

i. the OR gate whereby any input causes the output to occur;
ii. the AND gate whereby all inputs need to occur for the output to occur;
iii. the voted gate, similar to the AND gate, whereby two or more inputs are needed for the output to occur

Examples of the graphics used are shown in Table 2.3 and more detailed ones are used in more complex FTA.

Table 2.3 : Logical gates used in Fault Tree Analysis

	In an AND Gate, both events (A and B) have to occur in order for C to happen.
	In an OR Gate, if either event (A or B) occurs C will happen.

The advantages of this methodology includes the simple manner in which the tree can be produced and followed; its applicability to identify control measures; its ability to focus on multiple causes and the ease of extending into QRA. However, FTA requires experience, time and the tree may grow rapidly, hence adding complexity to analysis. Wang (2004) noted that Fault Trees built by different individuals for the same process are usually different in structure and may thus lead to different results. FTA method requires slight more time (Table 2.5) compared to ETA method (CCPS, 1992).

In efforts to address the problem of scarce information about reliability data of protection equipment and to improve time required to develop a full FTA, Hauptmanns (2004) developed and demonstrated the semi-quantitative fault tree analysis system (SQUAFTA). This new approach has proven that it can offer considerable savings in time when performing the analysis without sacrificing the advantages of the thorough fault tree analysis with regard to safety improvements.

2.1.4 Event Tree Analysis (ETA)

The ETA methodology is, to certain extent, the opposite of FTA as it begins with initiating events and builds up to the accident. It is an inductive reasoning process unlike FTA which is deductive (CCPS, 1992). ETA begins with initiating events leading to potential accident. Initiating events can include equipment failure, human error and process disturbances. The tree is constructed with initiating event on the left and then branching out to control measures. Failure or success states are defined for each control measure.

Figure 2.1 gives an example of an ETA, which can provide probabilistic type of output.

ETA methodology is a forward thinking process, which identifies development of accidents. The methodology is best suited for analyzing complex processes involving several layers of safety systems or emergency procedures (Wentz, 1990). It is useful in identifying control measures and useful in situations with varied outcomes. If data is available, ETA can be extended into QRA. However, the trees in ETA method, like FTA, can grow rapidly and there is possibilities of missing branches during calculation. However sums of all the event frequencies resulting from an ETA has to equals to one. This is one way of check and balance.

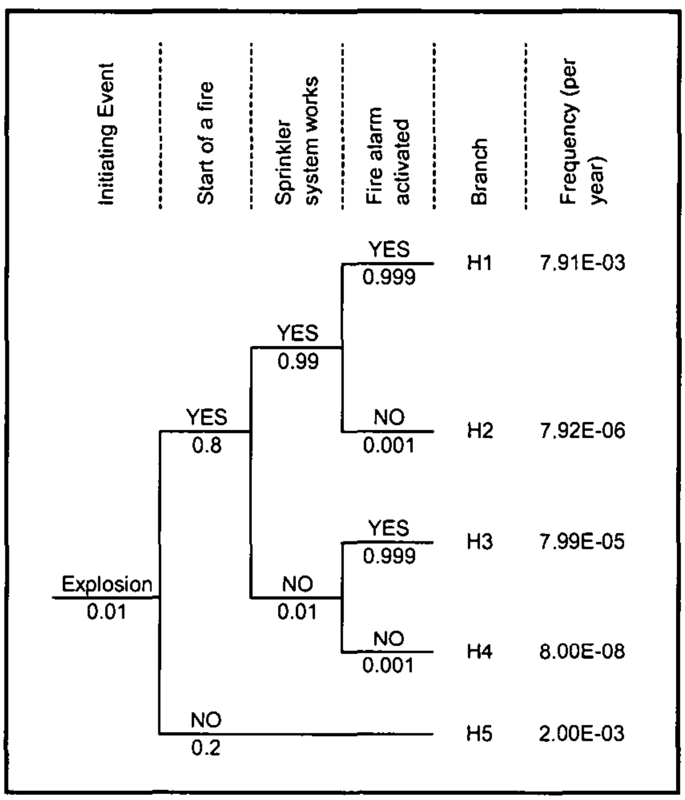


Figure 2.1 : Example of an Event Tree Analysis

An ETA can only be applied in cases where the outcome can only be YES or NO (Smith, 2003). The options are connected by paths, either to decision boxes or to outcomes. Calculation is only by multiplication.

Nivolianitou et. al. (2004) compared the ETA to FTA by applying them to the same accident. Their paper concluded that the ETA technique is able to represent the agents of a failure better than FTA and recovery from error in ETA is easier. Smith (2003), who made similar comparison, noted that ETA is more suitable to model event that happens in sequential manner. He also documented other differences between ETA and FTA as follows:

Table 2.4 : Comparison of ETA and FTA (Smith, 2003)

Event Tree	*Fault Tree*
Easier to follow for non-specialist	Less obvious logic
Permits several outcomes	Permits one top event
Permits sequential events	Static logic (implies sequence is irrelevant)
Permits intuitive exploration of outcomes	Top-down model requires inference
Permits feedback	No feedback
Fixed probabilities	Fixed probabilities and rates and times

2.1.5 Failure Modes and Effects Analysis (FMEA)

The FMEA is a systematic study of causes of failure and effects on the technical systems. FMEA is a qualitative method, which identifies design areas needing improvement. FMEA is typically carried out in tabular manner in which components are listed along with their functions. Then failure modes, failure rates, failure effects are analyzed. Failure detection and preventive measures are often the outcome from FMEA. An advanced method from FMEA includes criticality analysis of each component of the system. This variation is known as the Failure Modes, Effects and Criticality Analysis (FMECA). Both the FMEA and the FMECA are simple to carry out as they do not require any mathematics and their results are easy to interpret.

2.1.6 Relative Ranking

CCPS (1992) describes Relative Ranking as a method suitable for evaluation by comparing the hazardous attributes of chemicals, process conditions and operating parameters during conceptual design stage. There is no single method to perform Relative Ranking exercise and users can choose to develop own numerical index customized to their needs. However CCPS (1992) recommends that the numerical index for this purpose needs to factor in chemical and physical properties as well as process conditions. Numerical index should also be based upon known theoretical relationships or empirical correlations among parameters.

Inherent Safety indices developed up to this point (as deliberated in Sections 2.7.1 to 2.7.3) by Edwards, Heikkilä and Palaniappan are clear examples of indices which are developed to reflect degree of hazard inherent to the design and used to relatively rank process routes. This present research adopts similar approach and development of a two tier index will be deliberated in Section 4.1.

Each of the hazard identification techniques described above need varying manhours and they are suitable for different phases of the plant lifecycle. Table 2.5 provides typical manhours required for application of various techniques described above. Figure 2.2 shows the applicability of the hazard analysis techniques during the various phases of a process plant lifecycle.

Table 2.5 : Manhours of hazard and risk analysis techniques (CCPS, 1992)

Hazard and Risk Analysis Techniques	**Typical man hours required**
Hazard and Operability (HAZOP)	184 to 536
Failure Mode and Effects Analysis	176 to 416
Fault Tree Analysis	368 to 728
Event Tree Analysis	312 to 552

CCPS (1992) summarized the applicability of the techniques in various phases of the process plant lifecycle.

Process Plant Lifecycle	Hazard Evaluation Techniques				
	HAZOP	FMEA	RR	FTA	ETA
R&D	No	No	Yes	No	No
Conceptual Design	No	No	Yes	No	No
Pilot Plant Operations	Yes	Yes	No	Yes	Yes
Detailed Engineering	Yes	Yes	No	Yes	Yes
Construction / Start Up	No	No	No	No	No
Routine Operations	Yes	Yes	No	Yes	Yes
Expansion or Modification	Yes	Yes	Yes	Yes	Yes
Incident Investigation	Yes	Yes	No	Yes	Yes
Decommissioning	No	No	No	No	No

Notes :

HAZOP - Hazard and Operability
FTA - Fault Tree Analysis
RR - Relative Ranking
FMEA - Failure Mode and Effects Analysis
ETA - Event Tree Analysis

Figure 2.2 : Hazard analysis techniques in plant lifecycle (CCPS, 1992)

2.2 Quantitative Risk Assessment (QRA) In Process Plant Lifecycle

CCPS (1999) defines risk as a measure of human injury, environmental damage or economic loss in terms of both the incident likelihood and the magnitude of the loss or injury. The Health and Safety Executive UK (2001) refers risk as the chance that someone or something that is valued will be adversely affected in a stipulated way by the hazard. Kavianian and Wentz (1990) once proposed risk as a mathematical function as follow:

$$risk = probability \; x \; consequences \qquad \text{Equation 2-2}$$

Many more definitions of risk (CCPS, 1999) had been proposed and used to certain extent including the following:

a. Risk is a combination of uncertainty and damage
b. Risk is a ratio of hazards to safeguards
c. Risk is a triplet combination of event, probability and consequences

In all the definitions above, it can be concluded that in one way or another, risk has components of probability (uncertainty) of the event and consequences (effects) resulting from the event. It may be difficult to precisely quantify the risk parameters e.g. consequences of an explosion, so they must be estimated by adopting a systematic approach described in detail by Crowl and Louvar (1990) and Glickman and Gough (1990) in their works. The probability component is established mainly through years of observations and tests which culminated in publication of databases.

Over the last decade, QRA has gained a wide acceptance as powerful tool to identify and assess the significant sources of risk and evaluate alternative risk control measures in chemical process industries. QRA is part of Process Safety Management System (CCPS, 1999) which is considered a valuable tool in decision-making processes, to communicate among the experts involved, to quantify opinions and to combine these effectively with available statistical data. Lees (1996) in his review of various studies, concluded that QRA is an element that cannot be ignored in decision making about risk as it is the only discipline capable of enabling a number to be applied and comparisons to be made in quantitative manner. This technique is a systematic approach to identifying hazards, potentially hazardous events and estimating likelihood and consequences to people, environment and assets, of incidents developing from these events (Shell International Exploration and Production B.V, 1995). CCPS (1999) established a general guideline for QRA as illustrated in figure below.

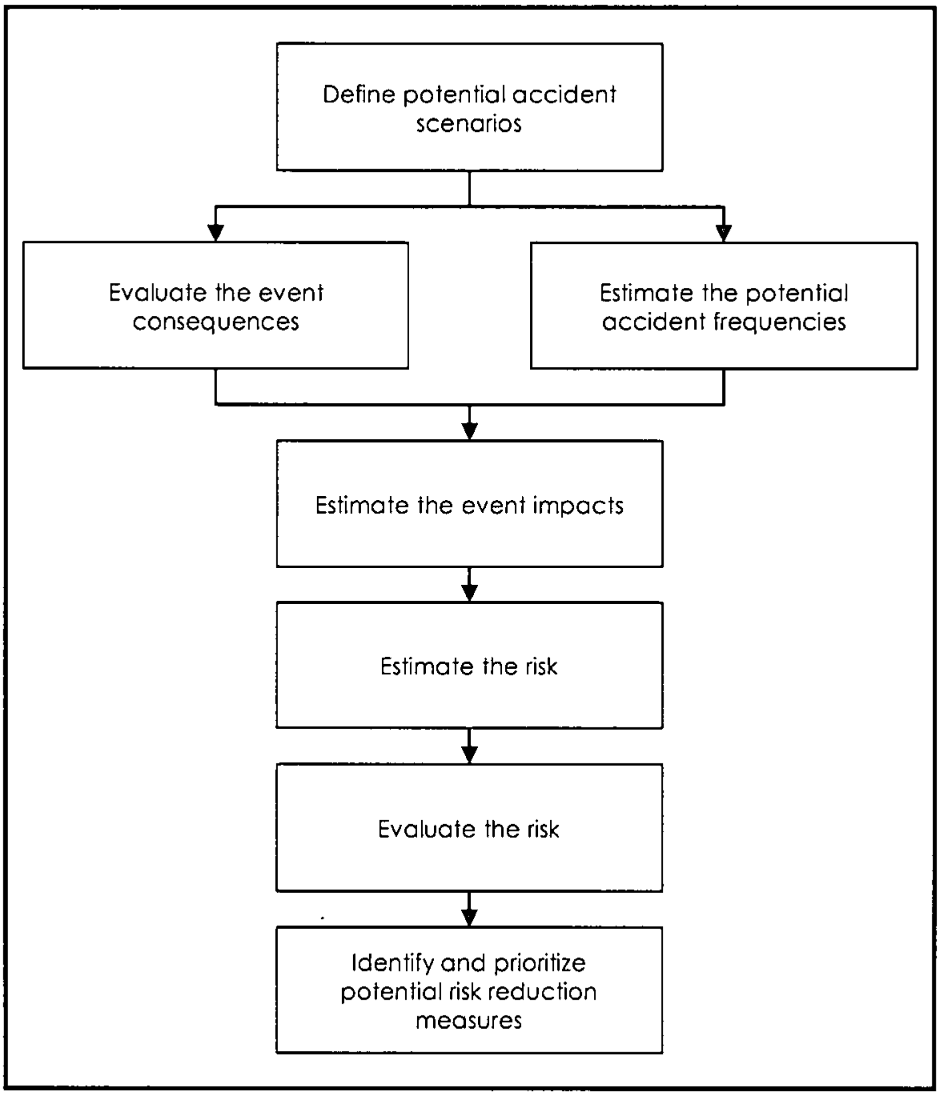


Figure 2.3 : Quantitative Risk Analysis flowchart (CCPS, 1999)

Lees (1996) on the other hand provided an expanded version of the QRA process in Figure 2.3 which has eleven steps. His expansion included identifying vulnerable targets (Step 4), determining possible escalation scenario (Step 6) and benchmarking estimated risk with established risk criteria (Step 10).

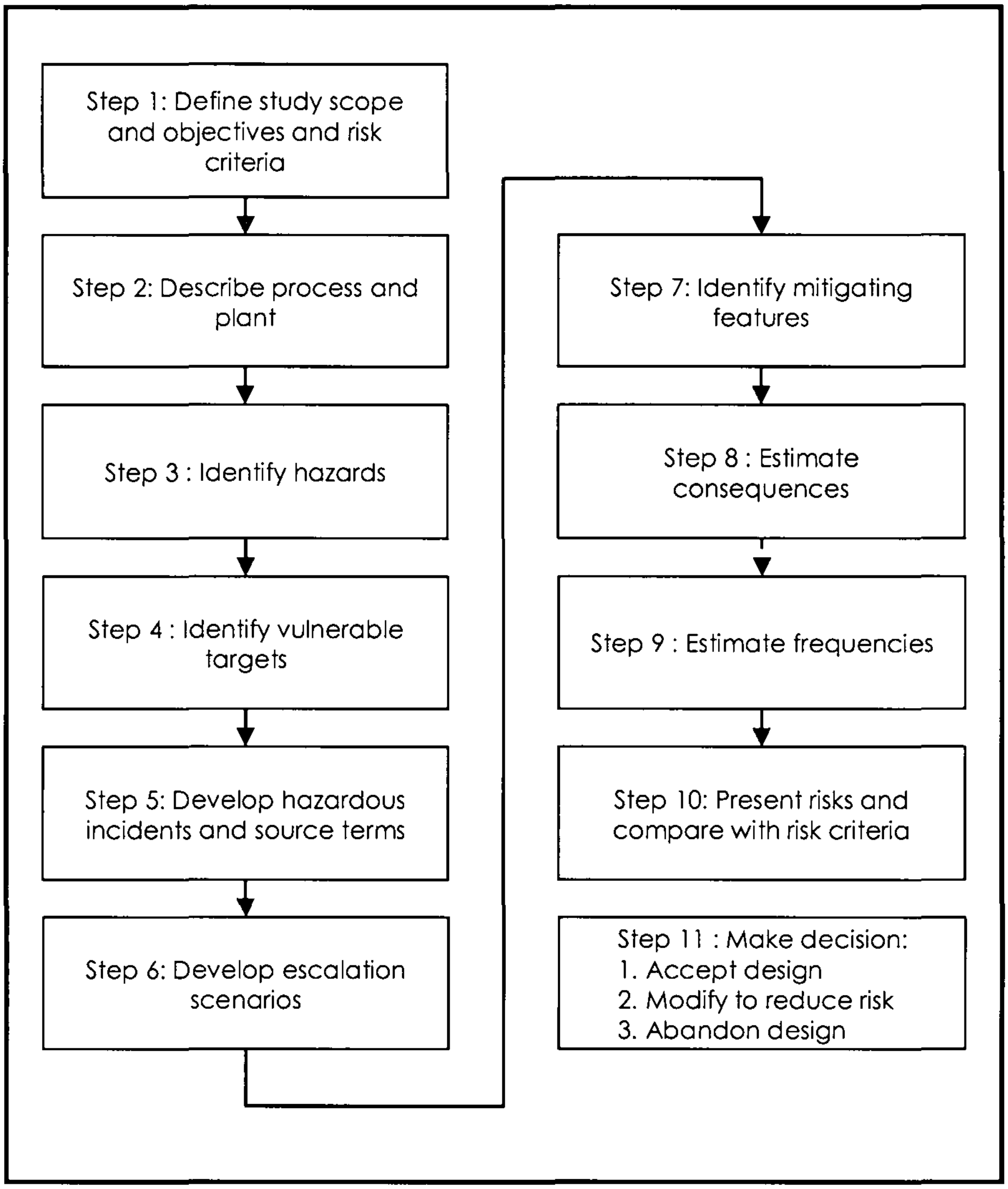


Figure 2.4 : Risk assessment process (Lees, 1996)

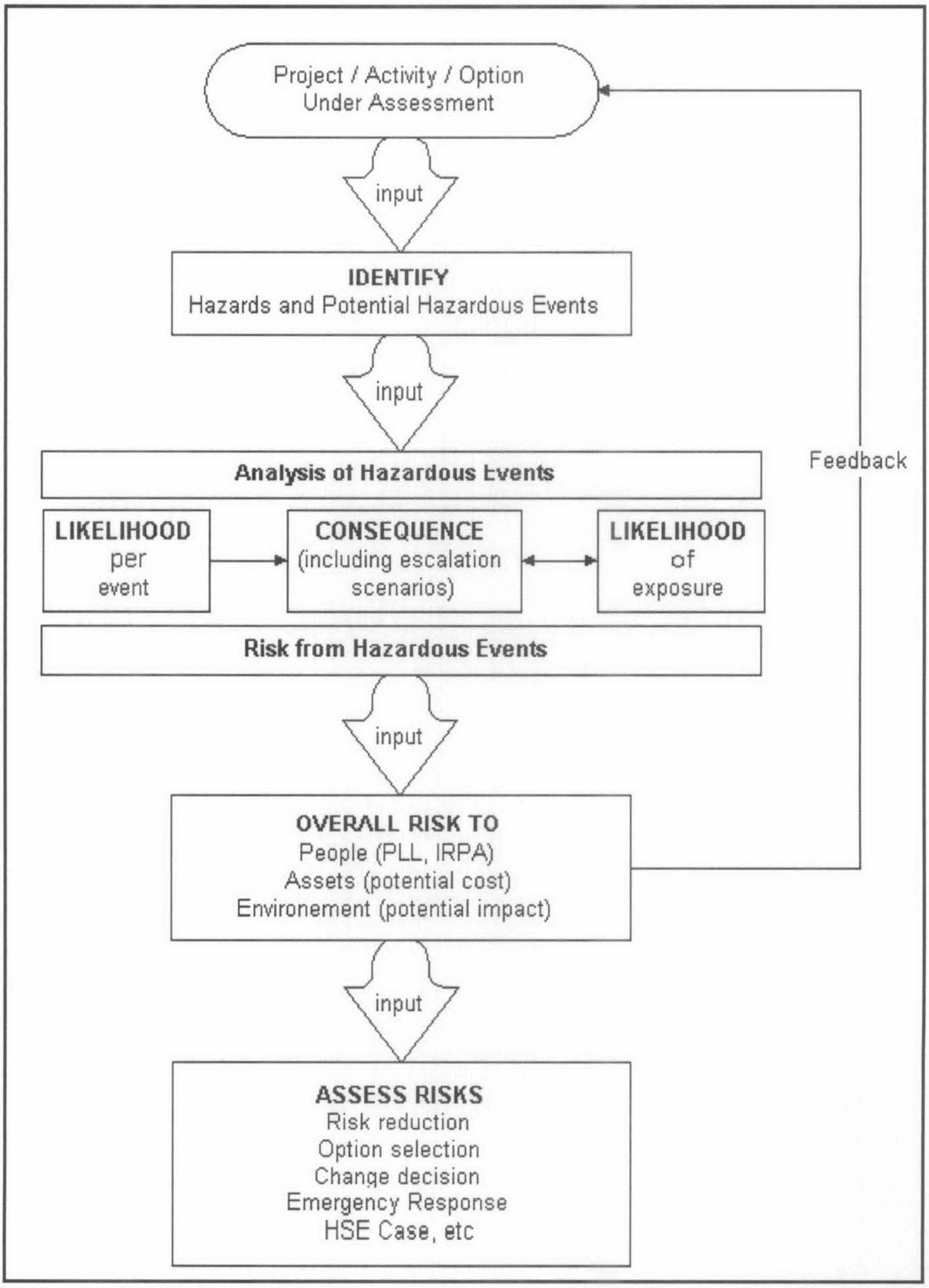


Figure 2.5 : Shell QRA Process (Shell, 1995)

In all the three QRA processes shown from Figure 2.3 to Figure 2.5, it can be observed that two major components are in common i.e. estimation of frequencies (probabilities) and the estimation of consequences. The three processes are also organized in similar sequence i.e. identify, estimate, compare, presenting results and decision making.

Similar to hazard identification techniques described in Section 2.1, the success of QRA depends on specialists, communication with others in the project, proper data handling i.e. selecting and using the most reliable and applicable data. It is important to note that QRA results should be used to reduce risk rather than to prove acceptability. QRA should be used to minimize risk to an As-Low-As-Reasonably-Practicable (ALARP) level rather than to a fixed number. The Principle of ALARP is further elaborated in Section 2.3. Each QRA must be tailored to specific project conditions to represent reality rather than force fitting into a rigid model. Lees (1996) noted that there are considerable variation between one QRA to another mainly due to the specific problems they try to address and the boundaries of the problems.

2.2.1 Application of QRA in Process Plant Lifecycle

Application of QRA has contributed to not only increased safety but also improved cost effectiveness in many areas (Shell International Exploration and Production B.V, 1995). Generally for a QRA to be meaningful, it is carried out after significant process design and main equipment layout tasks have been completed. QRA is desirable in, however not limited to only, cases where:

i. the exposures to the workforce, public, environment or the strategic value of the assets are high and reduction measures are to be evaluated
ii. equipment spacing allows significant risk of escalation (domino effects)
iii. new or novel technology is involved resulting in a perceived high level of risk for which no historical data is available
iv. demonstration of relative risk levels and their causes to the workforce to make them more conscious of the risks
v. demonstration to third parties, including government agencies and authorities, that risks are as low as reasonably practicable (ALARP)

QRA studies can be carried out in all stages of the project. However level of details and complexity differs, so do the uses of the QRA results. From Shell International Exploration and Production (SIEP) operating experience, QRA studies can take between 40 to 1500 man-hours depending on level of detail tabulated in Table 2.6

Table 2.6 : Manhours and deliverables of QRA (SIEP, 1995)

Man hours	Deliverables
40 to 200	In-house studies on several critical aspects of a facility or operation combined with an overall QRA on a cursory level along the interpretation of results in over all contexts.
300 to 600	Consultant studies with a similar scope as above but extended in detail
600 to 1500	Detailed evaluation of a facility by a consultant

Despite the manhours spent, it is important to understand that the methods like QRA cover only specific elements of the aspects involved in the safety of a plant. This method also requires subjective judgment and can only provide a partial idea about the safety present in a facility. The statistical methodology like QRA is rigorous but depend on data that in some cases are little more than guesses, since some events are too rare to allow the collection of statistically meaningful information. Combining data with a high degree of uncertainty will increase the uncertainty of the analysis information (Bowles and Pelaez, 1996).

In the UK, one of the principal applications of QRA in the process industries is in the safety case (Lees, 1996) while in Malaysia, the Control of Industrial Major Accident and Hazards (CIMAH) Regulations, 1996, require industries classified as Major Hazard Installation to submit a written Safety Report to the Director General at least three months before commencing the industrial activity (or before introducing hazardous substances into the plant). This Safety Report is a "life document" which requires updated version to be issued periodically and does not require approval. QRA is a component of Safety Report. In preparing QRA, any suitable method can be applied (International Law Book Services, 2000).

2.3 ALARP Principle and Frequency – Number (FN Curve)

The Royal Society Study Group (1992) noted several factors that influencing risk perception and hence acceptability including; (i) familiarity with the 'risk'; (ii) level of knowledge and understanding of the 'risk' or consequences or both; and (iii) the interplay between political, social and personal influences informing perceptions. From this, it can be inferred that the level of risk deemed acceptable to a certain group of population depends on how and what they perceive as risk.

In order to be reasonable within presently available technology and cost to minimize risk, a term known as As-Low-As-Reasonably-Practicable (ALARP) is used. This approach grew out of the so-called safety case concept first developed formally in the UK (Cullen, 1990). Hendershot (2002) iterated that the inherently safest case is the one with zero hazards, but this is a limiting and unachievable case. Therefore the objective should be to remove or reduce hazards subject to constraints dictated by technical and economic factors at that time.

The concept of ALARP is illustrated in Figure 2.6 based on definitions from UK HSE (2001), Lees (1996) and Shell (1995). The triangle represents the reduction of risk and there are three distinct regions. The top one being intolerable by any means. At the lowest end, the risk level is deemed to be acceptable. The region is between represents risk level that can be tolerated if efforts to reduce it to ALARP level can be shown. The numerical divisions of these regions are often expressed in "death per exposed individual per year" and defer from countries to countries. Some examples are tabulated in Table 2.7 from various references. The numerical divisions (known as individual risk) are determined for a person permanently placed at a fixed location (Withers, 1988).

Table 2.7 : Examples of numerical division of regions for risk acceptance

Country / Region	Individual Risk Criteria			Reference source
	Not tolerable	Tolerable with ALARP	Tolerable or broadly acceptable	
Russia	$>10^{-5}$	10^{-5} to 10^{-6}	$<10^{-6}$	Clark (2001)
Argentina	none	none	$<10^{-6}$	Clark (2001)
The Netherlands	$>10^{-6}$	10^{-6} to 10^{-8}	$<10^{-8}$	DNV (1993)
UK	$>10^{-5}$	10^{-5} to 10^{-6}	$<10^{-6}$	HSE (2001)
Western Australia	$>10^{-5}$	10^{-5} to 10^{-6}	$<10^{-6}$	DNV (1993)
Malaysia	10^{-3}	10^{-3} to 10^{-6}	$<10^{-6}$	DNV (1993)

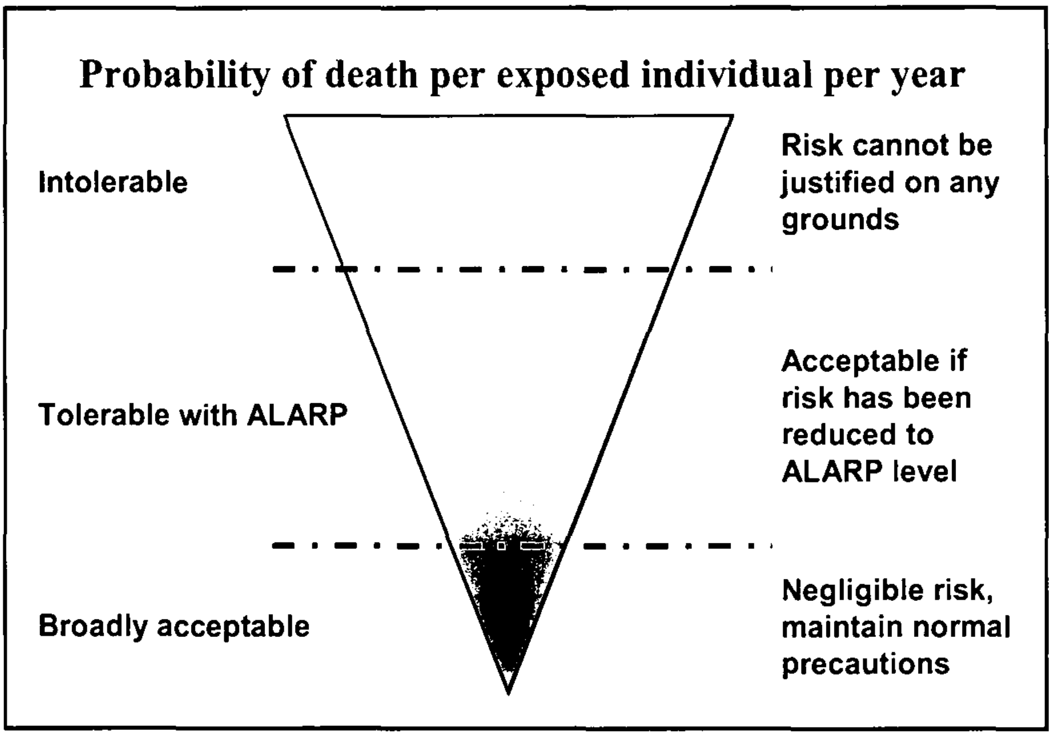


Figure 2.6 : Concept of ALARP

Societal risk measures the risk to a group of people (CCPS, 2000). Societal risk measures estimate both the potential size and likelihood of incidents with multiple adverse outcomes. Societal risk measures are important for managing risk in a situation where there is a potential for accidents impacting more than one person. HSE (2001) noted one way to determine proportionality for societal risks is to use the maximum potential fatalities (N). This value must be estimated as part of the 'assessment of the extent and severity of the consequences of identified major accidents' which is mandatory minimum information. The value of N can be combined with the frequency (F) of the event resulting in N to determine an indicator of societal risk levels. The combination of these two numbers when presented graphically is known as the FN curve. Hendershot (1999) noted that the FN curve is a common measure of societal risk. It is typically available in risk assessment software and usually forms part of risk assessment report. Many government agencies based their approval decisions on FN curve.

The illustrative FN curve, shown in Figure 2.7, is based on the ALARP principle discussed above and has three (sometimes more) regions. If the FN data for a particular plant falls into the highest region of "intolerable", the project is likely not to be approved until it can be proven that the FN data falls into the second segment of "tolerable if ALARP". In this case, the project has to demonstrate that it has necessary mitigation measures to make certain that the risk is ALARP.

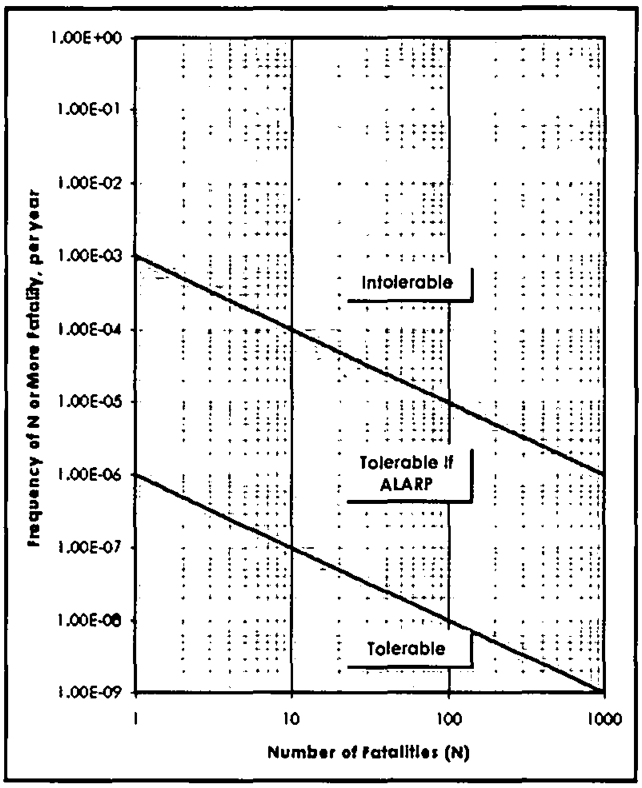


Figure 2.7 : Malaysian FN curve (DNV, 1993)

The numerical limits which cross the x and y axes and the slopes for the FN line differ from countries to countries similar to the definition of ALARP for individual risk. There are no universal upper and lower limits that can be used throughout (Lees, 1996). A survey conducted by DNV (1993) on the limits and slopes for FN curves for few countries, as tabulated below, demonstrates this point. Figure 2.7 has been plotted based on the data presented for Malaysia and is used throughout this research.

Table 2.8 : Limits and slope of FN curves

Authority	FN Curve Slope	Intolerable intercept with N=1	Negligible intercept with N=1	Limit on N
The Netherlands	-2	10^{-3}	10^{-5}	Nil
Hong Kong Govt.	-1	10^{-3}	Nil	1000
UK HSE	-1	10^{-1}	10^{-4}	1
Malaysia DOSH	-1	10^{-3}	10^{-6}	1

2.4 Frequency of Event and Probability of Fire and Explosion

Frequency is a measure of the likelihood of a particular accident and outcome occurring, and is measured as the number of occurrences per unit time (CCPS, 2000). One of the methods to determine frequency of an event is the Event Tree Analysis (ETA). Based on conclusions by Smith (2003), for an explosion incident, which is a result of a sequence of smaller events, ETA is the better choice compared to FTA to model it. Hendershot (1999) provided an illustration by using the ETA method, shown in Figure 2.8.

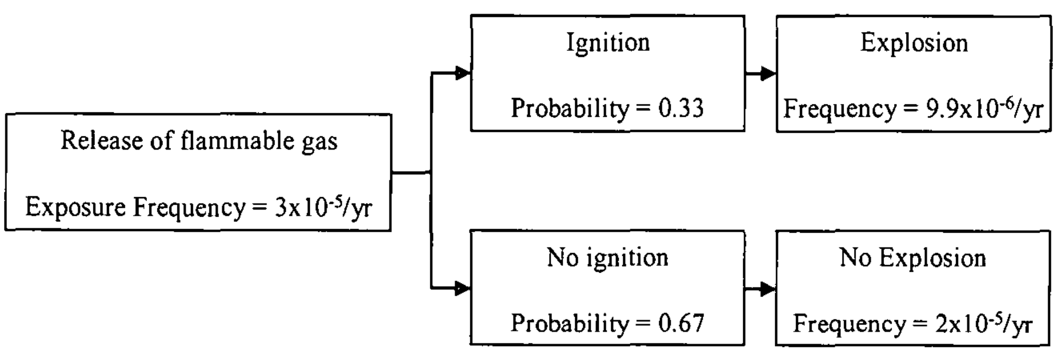


Figure 2.8 : ETA to determine frequency of event (Hendershot, 1999)

In this illustration, the frequency of an explosion resulting from a particular release of flammable gas is 9.9×10^{-6} per year. Exposure frequency is a function of base failure frequency of given piece of equipment multiplied by duration (usually in year) and exposure unit. The frequencies of such failure are often documented by actual operations of the equipment and usually are proprietary to the manufacturer. Modern risk assessment software typically has a set of generic base failure data built-in. An example is provided here by using base failure rate data from Cox et. al. (1990) to determine exposure frequency of a 25mm rupture leak in one year for a 5m pipe. Additional base failure rate from Cox (1990) is provided in Appendix B.

exposure frequency = base failure frequency x length x duration

$= 1\text{x}10^{-6}$ (failure year^{-1} m^{-1}) x 5(m) x 1 year

$= 5\text{x}10^{-6}$ per year

The ETA in Figure 2.8 can be further expanded to include influence of secondary events and human errors as a factor leading causing or adverting an explosion. Table 2.9 by Cox et. al. (1990) gives three examples of possible human error under high stress condition, for instance during a hydrocarbon leak in process plant.

Table 2.9 : Probability of human error (Cox et. al, 1990)

Possible types of human error	Probability
Operator fails to act correctly in the first 5 minutes after the onset of extremely high stress conditions.	0.9
Operator fails to act correctly after the first 30 minutes under extreme stress.	0.1
Operator fails to act correctly after several hours under high stress.	0.01

Withers (1988) presented an analysis of probability of fire and explosion as a function of quantity of hydrocarbon leaked based on data from Wiekema (1983) and the Canvey Report published in 1978. The analysis took into account a total of 36 incidents which resulted in ignition and explosion. By using linear regression, Withers (1988) then produced a table documenting chances (probability) of ignition and explosion for specific release sizes (quantity) shown here:

Table 2.10 : Chances of Ignition and Explosion (Withers, 1988)

Release size (≤ tons)	Chances of ignition and explosion
5000	0.7
2000	0.5
1000	0.4
500	0.32
200	0.2
100	0.15
50	0.11
20	0.06

Release size (≤ tons)	Chances of ignition and explosion
10	0.04
5	0.025
2	0.012
1	0.006
0.5	0.003
0.2	0.001
0.1	0

The probability of explosion is used in conjunction with ETA to determine the overall frequency of an explosion. Calculations are provided in further details in Section 3.9.

2.5 Risk and Consequence Analysis Software

Risk and consequence assessment software is used to predict impact of incidents for wide areas like the entire petrochemical industrial site. Many QRA reports are prepared using models and results from this software. Typically risk assessment software such as Software for the Assessment of Flammable, Explosive and Toxic Impact (SAFETI) and Process Hazard Analysis Software Tool (PHAST) by Det Norske Veritas (DNV), and Fire, Release, Explosion and Dispersion (FRED) by Shell are used to generate risk contours. These contours identify the areas that may be potentially affected due to a predefined disaster like vapor cloud explosion at a certain condition. Results from these simulations often forms part of the safety report issued by project owners to the federal and local regulatory bodies. Major features offered by the software mentioned above are Unified Dispersion Models (UDM), tabulation of risk ranking, calculations of risk contours and FN curves.

Commercially available risk assessment software are based on established methods and validated, in some cases, with large scale experiments (Cambridge Environmental Research Consultants Ltd, 2002). These commercially available risk assessment software packages typically function in similar pattern, which is graphically illustrated in Figure 2.9. These software tools depend on many manual inputs of conditions to simulate, making the modeling efforts very tedious and time consuming. Due to the nature of data requirement, the commercially available software can only be meaningfully utilized when detail design information is available, often towards the end of detail design simulation shown in Figure 1.2.

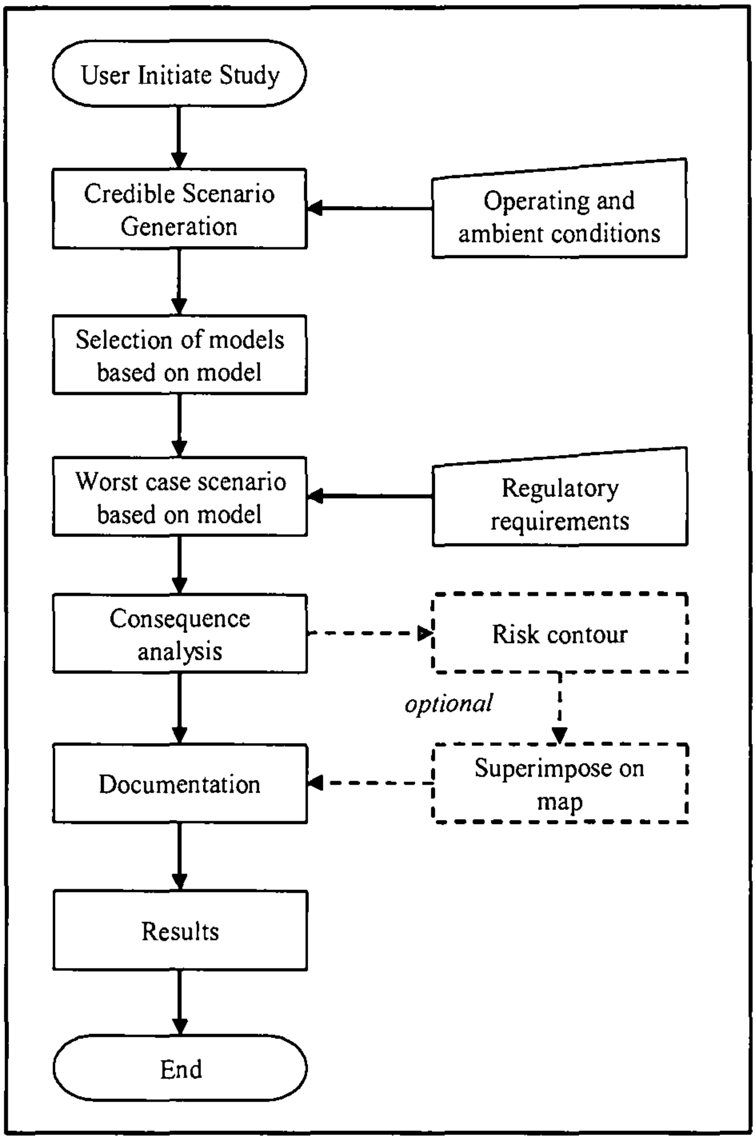


Figure 2.9 : Typical process flow of risk assessment software

2.5.1 Fire, Release, Explosion and Dispersion (FRED)

Shell developed a software suite for estimating risk of Fire, Release, Explosion and Dispersion. Models in FRED are used to predict the consequences of the accidental or design release of product from process, storage, transport or distribution operations. The models are validated by an extensive program of large-scale experiments, and the underlying methods have been published (Shell Global Solutions HSE Consultancy, 2001).

The FRED package provides an easy to use, traceable method for evaluating the consequences of user defined release scenarios. Plant designers, operators and safety engineers use these models to optimize equipment and layout options.

2.5.2 Process Hazard Analysis Software Tool (PHAST) Risk

PHAST Risk (formerly SAFETI) program is a user-friendly, industry standard method for carrying out Quantitative Risk Assessments (QRA) of onshore process, chemical and petrochemical facilities. PHAST Risk allows users to quickly identify major risk contributors (DNV, 2007).

PHAST Risk (Software for the Assessment of Flammable, Explosive and Toxic Impact) is by far the most comprehensive quantitative tool available for assessing process plant risks. It is designed to perform all the analytical, data processing and results presentation elements of a QRA within a structured framework. It analyzes complex consequences from accident scenarios, taking account of local population and weather conditions, to quantify the risks associated with the release of hazardous chemicals. It will calculate the risk associated with your installation and produce risk contours, FN curves and rankings of risk contributors. With this information, the safety of an installation against any risk criteria can be assessed and guidance obtained concerning possible mitigation measures, such as changes in design, operation, response or land use planning. Risk results are available graphically and may be overlaid on digitized maps, satellite photos and plant layouts (DNV, 2006).

Engineers in an operating plant often use PHAST to evaluate plausible accident scenarios. At the same time, tools like this can be applied to identification of dispersion patterns and exposure levels in unlikely events of leaks or ruptures in the plant.

2.5.3 Shell Code for Overpressure Prediction in Gas Explosions (SCOPE)

SCOPE is an explosion-screening tool developed by Shell based on mathematical models. It has been designed to quickly predict the likely overpressure generated by the accidental release and ignition of a gas cloud in a congested region of plant. It has been developed to calculate explosion overpressure using mixture of hydrocarbon gases and congestion factors to closely reflect actual situation of the plants (Puttock, 1998).

2.5.4 Integrating Inherent Safety Into Process Design

It is observed that none of the above mentioned software is connected to a process simulation tool. At such they are not able to produce risks contours or analyze consequences for varying operating conditions in a fast and efficient manner. Since there is no linkage between consequence analysis software and process simulation, manual data entry is often relied upon. This introduces room for data entry error and hence inaccurate results.

In addition, when process plant modifications are carried out, the possibility of redoing a detail risk assessment would be relatively low due to time and cost constraints. This is not desirable as new operating conditions may change risks levels related to the operations.

Mohd. Shariff et. al. (2006) proposed a feasible framework in which risk and consequences estimation can be part of design stages. A demonstrative tool named as integrated risk estimation tool (iRET) was developed by using HYSYS process simulation software and MS Excel spreadsheet as platforms.

iRET estimates risk due to explosions by using TNT Equivalence and the TNO Correlation methods. The paper also presented case studies which successfully shown that the risk due to explosion can be assessed during the initial design stage under varying process parameters. At such, modifications can be carried out within the HYSYS simulation, hence producing inherently safer designs.

The framework and iRET provided systematic methodology and technology to design inherently safer plants. iRET has the potential to be extended to include all forms of hazards such as fire, toxic gas releases and boiling liquid expanding vapor explosion (BLEVE). However it still lacks the ability to quantitatively compare the different designs as it does not have a mechanism similar to the indices reviewed in Sections 2.7.

2.6 Inherent Safety In Plant Design

In a typical approach to loss prevention, safety measures are engineered near the end of the design process, leaving add-on control measures to be the only option available (Khan and Amyotte, 2005). This approach alone is unable to avoid or reduce the risk of serious chemical accidents (Zwetsloot and Askounes-Ashford, 1999). This has been exemplified by the major incidents described earlier in this chapter. These protective measures added late in the design, often require regular preventive maintenance to detect revealed failures in order to prevent catastrophic events. The preventive maintenance throughout the life of the plant, adds to the operating cost as well as necessitating repetitive training and documentation upkeep.

The alternative to "traditional safety" measure is a measure which tries to avoid or eliminate hazards, or reduce their magnitude, severity or likelihood of occurrence by careful attention to the fundamental design and layout. Kletz (1991) formalized several principles (Table 2.11) defining Inherent Safety (IS). Inherent Safety is a proactive approach for hazard/risk management during process plant design and operation. Inherent Safety aims to reduce or eliminate the root causes of the hazards by modifying the design (hardware, controls, and operating conditions) of the plant itself instead of relying on additional engineered safety systems and features, and procedural controls which can and do fail. Inherent safety has become an important aspect and is deemed as the best method to design a plant safe for operation, with no harm to the environment and health.

Table 2.11 : General principles of Inherent Safety (Kletz, 1991)

Principles	**Explanations**
a. Intensification (minimization)	Reduction of the inventories of hazardous materials
b. Substitution	Change or hazardous chemicals substances by less hazardous chemicals
c. Attenuation (moderation)	Reduction of the volumes of hazardous materials required in the process. Reduction of operation hazards by changing the processing conditions to lower temperatures, pressures or flows.
d. Simplification	Avoidance of complexities such as multi-product or multi-unit operations, or congested pipe or unit settings
e. Limitation of Effects	The facilities must be designed in order to minimize effects of hazardous chemicals or energies releases.
f.	
g. Error Tolerance	Making equipment robust, processes that can bear upsets, reactors able to withstand unwanted reactions, etc.

Based on the above general principles of Inherent Safety, a number of researchers developed the following more definitive guidelines:

Table 2.12 : Definitive guidelines of Inherent Safety

Guidelines	**Explanations**
Avoiding knock-on effects	Ample layout spacing, fail-safe shut down, open construction
Making incorrect assembly impossible	Unique valve or piping systems to reduce human error
Making status clear	Avoidance of complicated equipment and information overloading
Ease of control	Less hands-on control

Amyotte et. al. (2007) argues that inherent safety principles should be applied right after hazards are identified and before add-on safety features are to be considered. They provided an illustration by applying the principle of attenuation or moderation to mitigate dust explosion. Their paper however, did not discuss the cost impact of such modification.

Applications of inherent safety can lead to enhanced safety and lower capital and operating costs (CCPS, 2001; Edwards and Lawrence, 1993; Hendershot, 2000). The inherent safety approach uses basic design measures to achieve hazard elimination, prevention and reduction.

In terms of cost, any re-design done after the detailed design stage of the process lifecycle would be very expensive compared to alteration in the early stage i.e. during conceptual design stage. Khan and Amyotte (2002) reflected similar finding in their work, which stated that, considering the lifetime costs of a process and its operation, an inherently safer approach is a cost-optimal option. This is further substantiated by the their work showing that Inherent Safety can be incorporated at any stage of design and operation; however, its application at the earliest possible stages of process design (such as process selection and conceptual design) yields the best results. Also, modification would also be easily implemented at that stage.

It has been shown that Inherent Safety does not end at the invention phase and should be applied through the lifecycle of the plant. The largest payoffs are achieved by verifying that inherent safety principles have been considered early and often in the process and engineering design sequence (Warwick, 1998 and Crawley, 1995). It has also been proven (Zwetsloot and Askounes-Ashford, 1999) that inherently safer options are also economically and technically viable for operating plants.

Although it is an attractive and cost-effective approach to hazard/risk management, inherent safety has not been used as widely as other techniques such as Hazard and Operability (HAZOP) studies and Quantitative Risk Assessment (QRA). There are many reasons responsible for this; key among them are a lack of awareness and the non-availability of a systematic methodology and tools (Khan and Amyotte, 2002).

2.6.1 Challenges Of Implementing Inherent Safety In Industries

Despite the attractiveness of being able to proactively identify and reduce risk, the principles of Inherent Safety have not been widely adopted in the industries. The lack of experience and knowledge (field and "real world plant") of the designers who are applying these principles and the lack of recognized methodology to review the agreement of different process alternatives according to the Inherent Safety principles are the crucial obstacles to the implementation of this safety philosophy (Moore A.D., 1999). Another worker in this area, Harstad (1991) had emphasized safety as an integral part of the various stages of plant (platform) design. Several examples of this approach were given but no systematic methodology or guidelines were proposed to conduct such integrated design.

Perhaps another difficult part of implementation would to convince stakeholders and/or process owners about the benefits of investing in Inherent Safety features. Process designers are often faced with the question, "How can the benefits of Inherent Safety features be being quantified?" Quantification is a challenge because there is no definitive comparison unless two identical plants of similar design were built, with one using Inherent Safety feature and the other one without. The other reasons are summarized by Kletz (1991) in his work shown in Figure 2.10.

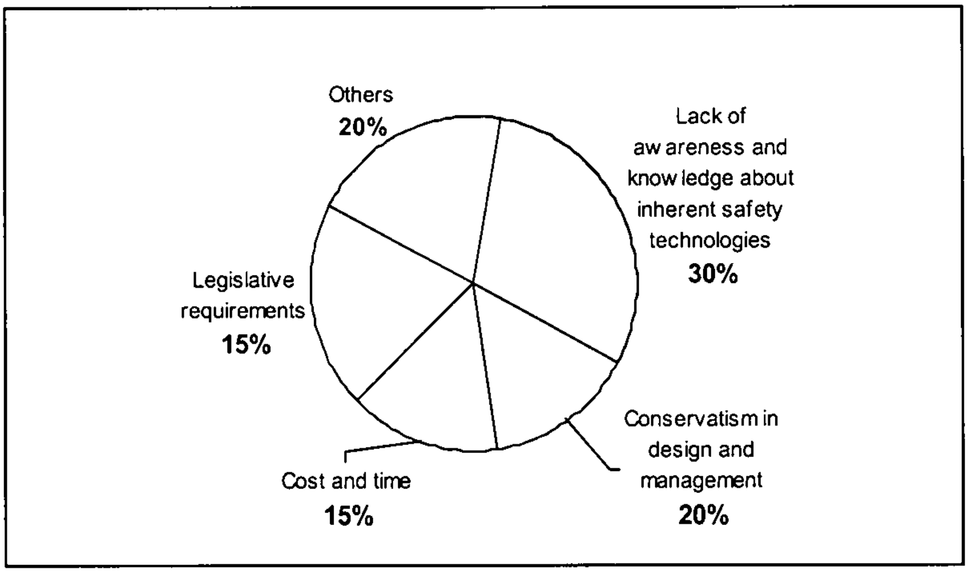


Figure 2.10 : Problems of Implementing Inherent Safety (Kletz, 1991)

Apart from Kletz's work, a number of other studies had been carried out to ascertain application of Inherent Safety Principles in process design. One study by Mansfield, Kletz, and Al-Hassan (1996) assessed the familiarity and application of inherent safety among designers and companies. This study observed that although many designers know of the basic principles of inherent safety, they are not always clear about how to apply them. There is also a general lack of familiarity with the specific advantages of adopting an inherently safer approach to process design.

Rushton et al. (1994) emphasized the need for a computer aid that will perform comprehensive inherent safety analysis at each key decision point in the process life. The key benefits of automation are substantial reduction in time and effort, enhanced decision-making, improved documentation, and better understanding of the process.

2.7 Quantification of Inherent Safety Level (ISL)

A number of researchers worked to address the problems related to quantification of Inherent Safety Level (ISL). Chronologically, the first published work was "Quantifying inherent safety of chemical process routes", Ph.D. Thesis, Loughborough University, Loughborough, UK, (Lawrence, 1996); "Inherent safety in process plant design", Ph.D. Thesis, VTT Publication Number 384, Helsinki University of Technology, Espoo, Finland, (Heikkilä, 1999). These researches introduced the fundamental concept of ranking chemical process routes based on indices that are functions of pressure, temperature, composition and so on. The individual techniques are discussed in further detail in following sections.

Subsequent researches focused on improvement of the indices proposed by Lawrence (1996) and Heikkilä (1999). Palaniappan (2002) improved the original index systems while Gentile (2004) proposed a fuzzy logic based Inherent Safety Index. Gupta and Edwards (2003) developed a graphical method to measure ISL.

The latest published work on ISL quantification is by Khan and Amyotte (2005) who attempted to address the concerns by various prior researchers who noted that non-availability of effective tools for inherent safety evaluation as one of the major limiting factors restricting the application of inherent safety (Section 2.6.1)., Khan and Amyotte (2005) proposed a structured guideword based approach similar to the well-known and practiced HAZOP study procedure named the "integrated inherent safety index (I2SI). This index was intended ultimately to be applicable throughout the lifecycle of process design.

Each of these indices were critically reviewed and presented in separate sections below followed by a comparison of these indices and recommendations for improvement.

2.7.1 Prototype Index for Inherent Safety (PIIS)

In his Doctoral thesis, Lawrence (1996) developed, a prototype index for ranking alternative chemicals routes based on inherent safety characteristics of the alternatives. The prototype index was initiated back in 1993 and incorporated 7 parameters about physical properties of chemicals, and conditions of reaction steps. For each of these parameters, the researcher developed scoring tables that were used to evaluate each process alternative.

The researcher tested the prototype index using a number of routes to produce methylmethacrylate (MMA). Each route is evaluated against the process score, which evaluates the temperature, pressure and reaction yield. Subsequently, the routes are evaluated against hazards due to the properties of chemicals, which are inventory, toxicity, explosiveness and flammability. This is known as the chemical score.

Since this work was the pioneering work, the prototype index was verified by a panel of experts who ranked the alternative routes independently. The experts consisted of academicians and industrial practitioners who are reputable in the field of inherent safety. Lawrence (1996) assumed that the experts' opinion and experience of inherent safety would be worthy of consideration. Experts consulted by Lawrence (1996) include the following:

1. Professor F.P. Lees, Loughborough University
2. Professor H.A. Duxbury, Independent Consultant / Loughborough University
3. Dr. T.A. Kletz, Independent Consultant / Loughborough University
4. Dr. A.G. Rushton, Loughborough University
5. C.C. Pinder, BP Chemicals Ltd., / Loughborough University
6. M.L. Preston, ICI Engineering
7. M. Kneale, Independent Consultant
8. W.H. Orrell, Independent Consultant

These experts were given questionnaires pertaining to the process routes and were asked to rank them accordingly. Interviews and discussions were also conducted to obtain their feedback and suggestions to improve the research. The ranking from the experts agreed closely to the ranking produced by the prototype index calculations.

The prototype index had four major problems i.e. inventory estimation and scoring, arbitrary division of parameter ranges and scores, simplified parameter weighting and combination, methodology to combine process step scores. Lawrence (1996) then improved the prototype inherent safety index by proposing a four factors structure shown here:

*Inventory * hazard assessment * probability of release * effects modifier*

"...the '*' means 'combined with in some way' and not necessarily multiplication. These combining functions will depend upon how the factors are structured. For example, if they are all scores then addition is most appropriate, whereas if inventory is in ton and hazard assessment is in hazard per ton then multiplication is more appropriate..."

Rahman et. al. (2005) noted the index developed by Lawrence is very reaction-step oriented and does not consider for example, separation sections at all. This index does not consider reaction hazards directly but through yields, operating conditions and physical properties. However, it is very straightforward and fast to use, since all the input data can be found from material safety data sheets and process literature. The index does not treat a process stream as a mixture but rather assesses individual chemicals used in the reactions. This does not reflect actual process condition where content in a stream is more often that not, a mixture.

Lawrence (1996) further investigated the possible correlation of ISL in process route to cost. By applying statistical analysis it was concluded that level of inherent safety is strongly related to the number of process steps. The more process steps, hence more complexity in a route, will result in lower ISL. The analysis also shown that ISL is not significantly correlated to capital costs nor production cost alone. However, when the cost of production includes more capital related costs, for example direct cash (maintenance, overheads, etc.) and full cash (insurance and property tax), the correlation is significant. There was insignificant correlation between cost of raw materials and level of inherent safety.

2.7.2 *Inherent Safety Index (ISI) In Process Plant Design*

Heikkilä (1999) proposed and developed a more structured manner to assess level of inherent safety. The doctoral thesis proposed the overall index as summation of the chemical inherent safety index and the process inherent safety index. Each of these indices further consists of sub-indices provided in Table 2.13. This set of indices has 12 parameters versus 7 proposed by Lawrence (1996). The score range for each index is also smaller, hence easing judgment by users. Detail definition for each sub index is deliberated in the thesis. Case studies based on acetic acid process routes were carried out to illustrate the concept and applications.

Table 2.13 : Inherent safety sub indices (Heikkilä, 1999)

Chemical inherent safety index	*Score*	*Process inherent safety index*	*Score*
Heat of main reaction	0 to 4	Inventory	0 to 5
Heat of side reaction, max	0 to 4	Process temperature	0 to 4
Flammability	0 to 4	Process pressure	0 to 4
Explosiveness	0 to 4	Equipment safety – ISBL	0 to 4
Toxicity	0 to 6	Equipment safety – OSBL	0 to 3
Corrosiveness	0 to 2	Safety of process structure	0 to 5
Chemical interaction	0 to 4		
Note : ISBL – Inside Battery Limits, OBSL – Outside Battery Limits			

ISI has the largest set of sub-indices. The advantage is in the more accurate results. The setback is in the effort to obtain more information. For this method to work well, the process diagram is needed for the equipment index and inventory, since the inventory index is based on the real number of equipment.

The score range corresponds to the expected impact of the parameter to plant safety. According to Heikkilä, a wider score range for instance, 0 to 6 for toxicity means toxicity has a greater impact to plant safety. The scores for each parameter are mainly based on previously established classification by other researchers and/or organizations. For instance, Table 2.14 shows that the score for flammability is based on European Union Directive (Heikkilä, 1999).

Table 2.14 : ISI score for flammability (Heikkilä, 1999)

Flammability classification	Score
Non flammable	0
Combustible (flash point >55°C)	1
Flammable (flash point < 55°C)	2
Easily flammable (flash point <21°C)	3
Very flammable (flash point <0°C and boiling point <35°C)	4

On the other hand, some scores, for instance explosiveness, seemed to be arbitrarily assigned.

Table 2.15 : ISI score for explosiveness (Heikkilä, 1999)

Difference in UEL – LEL (%)	Score
Non explosive	0
0 – 20	1
20 – 45	2
45 – 70	3
70 – 100	4

2.7.3 Expert System For Inherently Safer Chemical Processes (i-Safe)

By adopting methodologies from Lawrence (1996) and Heikkilä (1999), Palaniappan (2002) from National University of Singapore, developed a software tool known as i-Safe to analyze inherent safety of process routes in his M. Eng. thesis. Apart from the computer software tool, the thesis also proposed three additional supplementary indices – worst chemical index (WCI), worst reaction index (WRI), and total chemical index (TCI) to overcome shortcoming in earlier indices.

The WCI is the summation of maximum values of the flammability, toxicity, reactivity, and explosiveness indices of all the materials involved in a reaction step. Similarly, the WRI is the sum of the maximum of the individual indices of temperature, pressure, yield, and heat of reaction of all the reactions involved in the process. The TCI is a measure of the number of hazardous chemicals involved in the route. That is, a route with just one highly toxic chemical is safer compared to another route with several toxic chemicals. The application of i-Safe was carried out by evaluating ten routes to produce acetic acid.

Table 2.16 : i-Safe index calculations (Palaniappan et. al., 2002)

Component of inherent safety index	**Notation**	**Equations**
Individual chemical index	ICI	$N_r + N_f + N_t + N_e$
Individual reaction index	IRI	$R_t + R_p + R_y + R_h$
Hazardous chemical index	HCI	max(ICI)
Hazardous reaction index	HRI	max(IRI)
Overall chemical index	OCI	max(ICI)
Overall reaction index	ORI	ΣIRI
Overall safety index	OSI	Σ (OCI + ORI)
Worst chemical index	WCI	$\max(N_r) + \max(N_f) + \max(N_t) + \max(N_e)$
Worst reaction index	WRI	$\max(R_t) + \max(R_p) + \max(R_y) + \max(R_h)$
Total chemical index	TCI	ΣICI

Nomenclatures :

N_r NFPA reactivity rating
N_f Flammability index
N_t Toxicity index
N_e Explosiveness index
R_t Temperature sub-index
R_p Pressure sub-index
R_y Yield sub-index
R_h Heat of reaction sub-index

Comparing to early work by Lawrence and Heikkilä, i-Safe is also a reaction oriented index, which is quite easy to use. Similar to PIIS and ISI, i-Safe also evaluate the chemical as individual component and not as a mixture. Combined effects of process parameters are also not being represented by any of the indices thus far.

2.7.4 Graphical Method For Measuring Inherent Safety

In an effort to derive a simple to use ISL quantification technique, Gupta and Edwards (2003) proposed a graphical method to rank parameters of interest individually for each step in a process route without carrying out any mathematical operation and then be compared with each other. In Kletz's view, this benchmarking approach was seen as more acceptable to potential users.

The measurement procedure proposed by these two researchers can be used to differentiate between two or more processes for the same end product. The salient steps are: Consider each of the important parameters affecting the safety (e.g., temperature, pressure, toxicity, flammability, etc.) and the range of possible values of these parameters can have for all the process routes under consideration for an end product. Plot these values for each step in each process route and compare. No addition of values for disparate hazards (temperature, pressure, inventory, toxicity, flammability, etc.) is being suggested to derive an overall ISD index value since that conceals the effects of different parameters.

An example comparing six routes to produce methyl methacrylic acid (MMA) is provided in Figure 2.11. In this example, from the pressure perspective, the ACH route has significant advantage over the other five routes as this route operates at much lower pressure compared to the rest.

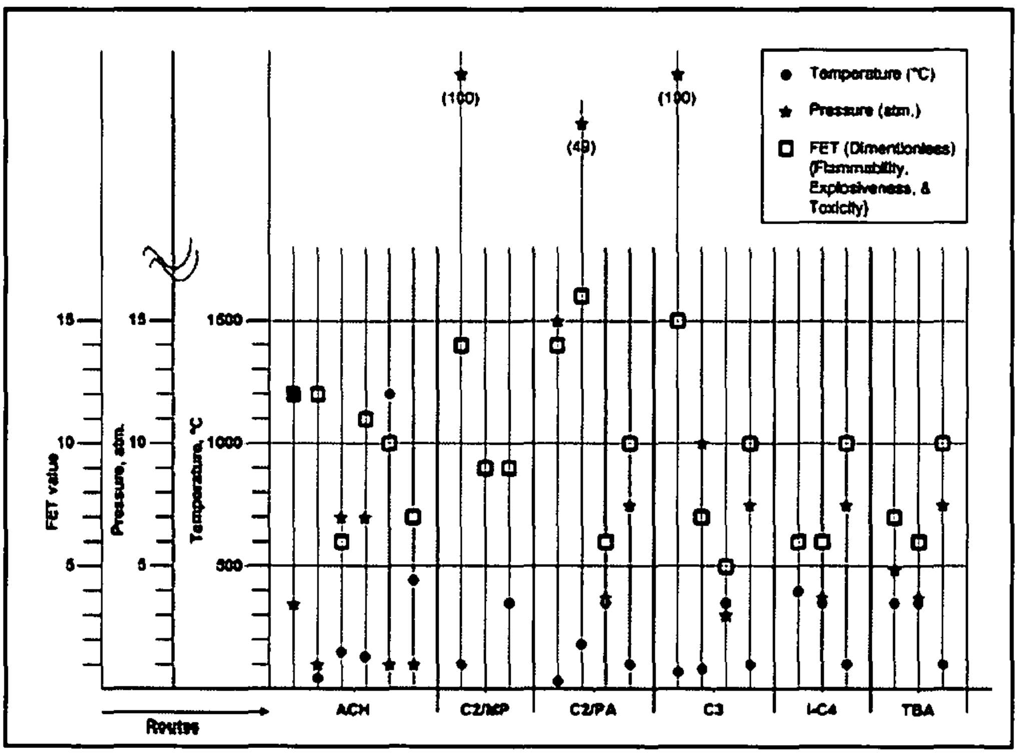


Figure 2.11 : Graphical ISL quantification method (Gupta and Edwards, 2003)

2.7.5 Hierarchical Fuzzy Model For Inherent Safety Evaluation

Gentile (2004) in her doctoral thesis developed a fuzzy logic based model to evaluate the level of inherent safety. Her research at the Mary Kay O'Connor Process Safety Center, Texas is based on applying fuzzy logics to the original index developed by Heikkilä (1999). The modifications were essentially aimed at improving the sensitivity (either excessive or insufficient) in the ranges selected for each of the various index parameters. The model is then applied to transportation of hazardous materials as a case study.

As noted by Gentile (2004) the fuzzy-based approach eliminates the problems presented by a traditional interval approach for parameter ranges and is seen as a first step toward a more reliable and simple methodology for inherent safety evaluation. Further work identified by the researchers includes: parameterization of inherent safety, unified membership functions, development of if–then rules, and reliable and robust methods of quantification.

2.7.6 Integrated Inherent Safety Index (I2SI)

Khan and Amyotte (2004) proposed a new indexing technique which is intended to be applicable throughout the lifecycle of process design. The conceptual framework of the Integrated Inherent Safety Index (I2SI) is illustrated in Figure 2.12.

The I2SI comprises of two main sub indices i.e. the hazard index (HI) and the inherent safety potential (ISPI) index. The HI is intended to be a measure of the damage potential of the process after taking into account the process and hazard control measures.

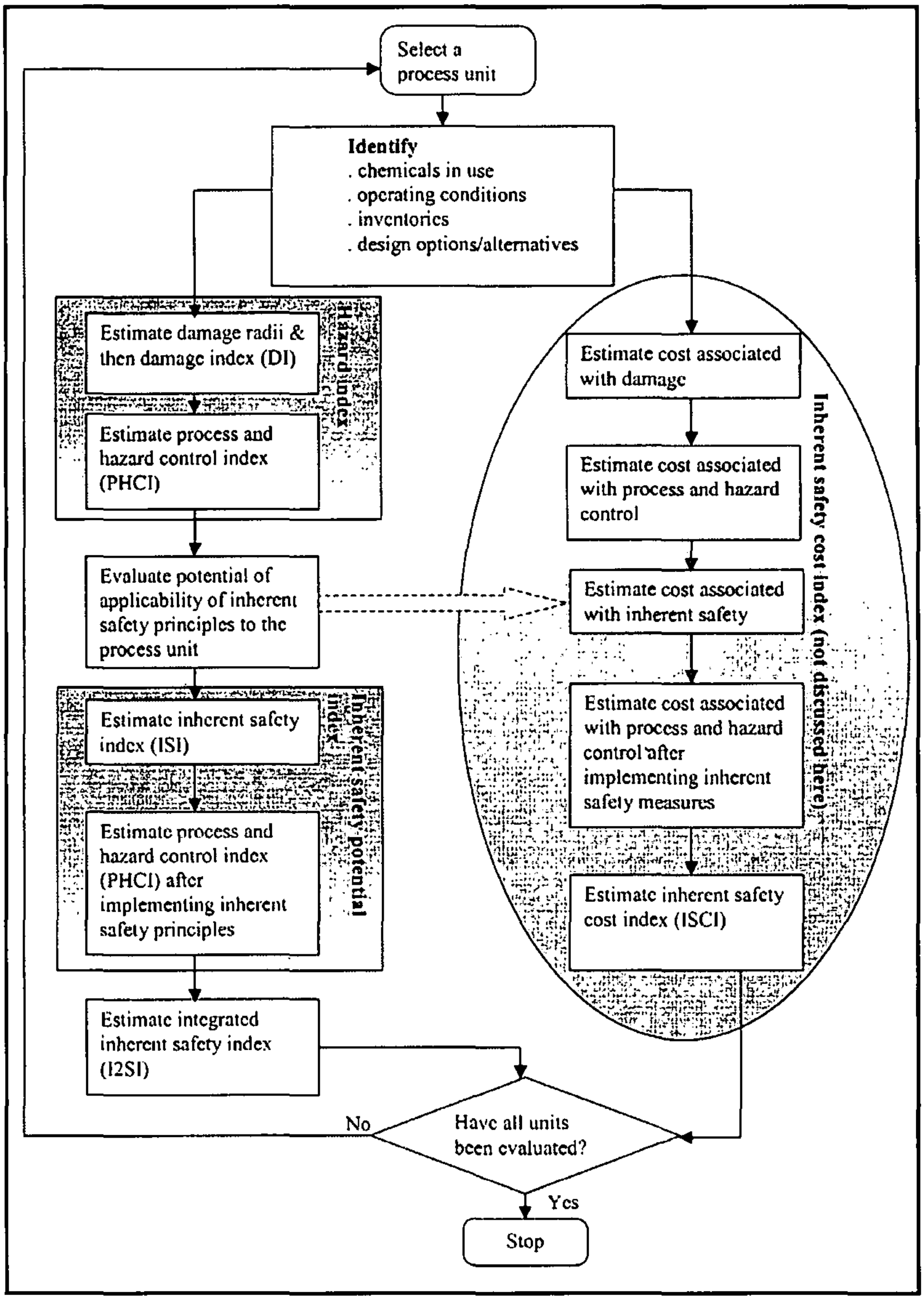


Figure 2.12 : Conceptual framework of I2SI (Khan and Amyotte, 2004)

The ISPI, on the other hand, accounts for the applicability of the inherent safety principles (or guidewords) to the process. The HI is calculated for the base process (any one process option or process setting will be considered the base operation or setting) and remains the same for all other possible options. The HI and ISPI for each option are combined to yield a value of the integrated index as shown in Equation 2-3.

$$I2SI = \frac{ISPI}{HI} \qquad \text{Equation 2-3}$$

Both the ISPI and the HI range from 1 to 200; the range has been fixed considering the maximum and minimum likely values of the impacting parameters. This range gives enough flexibility to quantify the index. As evident, an I2SI value greater than unity denotes a positive response of the inherent safety guideword application (inherently safer option). The higher the value of the I2SI, the more pronounced the inherent safety impact.

2.7.7 Status of Inherent Safety Level Quantification Research

The progress of the current works in quantification of inherent safety remains at the development of indices and the related improvements. None of the indices discussed in sections above have been adopted widely by the industries. In a survey involving 36 respondents from industries and consultants, 24 from academic and R&D organizations and 3 from regulatory bodies (Gupta and Edwards, 2003) concluded that the industry felt that the proposed methods are very elegant, yet too involved for easy adoption by the industry which is apprehensive of yet another safety analysis regime not yet mandated by law. Breakdown of respondents is provided in Table 2.17 below.

Table 2.17 : Responses received by country (Gupta and Edwards, 2002)

Name of country	Responders	Name of country	Responders
Canada	4	Japan	2
Denmark	1	Singapore	2
Finland	5	The Netherlands	2
Germany	1	United Kingdom	30
India	2	USA	13
Israel	1		

In the same survey, approximately 25% of the respondents stated that they were familiar with the concept of IS indices but had not used them because the IS indices were too complicated, require a lot of process data (manually), could not be used in early development stages and that a quicker method was needed.

In a recent work in 2005 by Rahman et. al., the 3 pioneering inherent indices (the PIIS, ISI and i-Safe) was compared using the methyl methacrylate (MMA) processes and weighted against expert opinion. The work concluded that inherent safety evaluations can be made in a reasonable accuracy with the index methods discussed. The results for sub process evaluation using the indices deviate between 10 to 15% from expert opinion depending on which index was used. The results of process route evaluations defer between 4 to 10% from expert opinion depending on index used. It was also noted that ISI by Heikkilä, which is more comprehensive and elaborate to use, gives more accurate results.

Rahman et. al. (2005) also noted that the PIIS is the most straightforward to use method, despite not considering reaction hazards directly. i-Safe includes direct reaction hazard evaluation through heat of reaction and reactivity rating but it does not have direct inventory or process equipment related indices. Still the accuracy was not better than with PIIS in this case study.

The present author finds that the current indices lack the ability of reflecting the actual process stream conditions as the current indices treat chemical component as individual components and do not account for quantities of each component in the stream. The indices do not account of toxicity, flammability of the actual mixture. Instead, the toxicity and flammability are accounted for as individual components. This is further illustrated in Table 2.18.

Table 2.18 : Flammability Limits of Individual Components

Component	Mole Fraction	Lower Flammability Limit (LFL)	Upper Flammability Limit (UFL)	UFL – LFL	Heikkilä Explosiveness Classification
CO	0.41	12.5	74.2	61.7	3
Methanol	0.01	5.9	36	30.1	2
Acetic Acid	0.58	4	16	12	1

When calculated as a mixture (accounting for mole fractions of each component in the stream) the LFL of the mixture having the components above result in 5.576% and the UFL is 23.78%. The detail calculation is described in Appendix A. The UFL-LFL is therefore 18.21%. Basing on

Heikkilä's ISI (Table 2.15), the explosiveness index for this stream is 1 which is more reflective of the true situation of the stream i.e. as a mixture and not individual components. More over the current methods do no account of effects of temperature and pressure on LFL and UFL. The influences are discussed in Section 3.2.

Rahman et. al. (2005) also observed that all indices suffer to some extent from simplifications and lack of sub index interactions. In his review, he noted, for example, a large inventory of dangerous or harmless chemical affects the level of safety in reality. However, due to the lack of interaction between sub indices, both cases get the same inventory index values, since inventory does not consider the type of content.

The present research resonates similar opinion. From the literature cited in Sections 2.7.1 through 2.7.6 it is observed that current inherent safety indices account for potential hazard from the parameters individually and not the combined effect of these parameters. For instance, the amount of process chemical that is leaked to the environment is a function of pressure and density of the fluid not just pressure alone. This present research attempts to propose an index to reflect actual release scenario.

Further to this, the present indices are focused on quantifying the ISL based on reactions thus only allowing them to assess and differentiate process routes and not individual process streams within a route. Comparison at a stream level for selected process route is important especially when trying to prioritize improvement efforts.

It is in the opinion of this research that for Inherent Safety Level (ISL) quantification to gain wide acceptance in the industry the quantification process needs to be computerized and linked with commonly used software and to be able to account for the properties of the mixture rather than individual components. At such, the current research work recommends the integration of inherent safety quantification with process design software. A of this concept prototype of linking Inherent Safety Index with HYSYS process simulator has been developed by Chan and Mohd Shariff (2008) in their recent paper. The indexing methodology used in the prototype is based on Heikkilä's (1999) ISI described in Section 2.7.2 with an enhancement whereby the process streams are treated as a mixture and not individual components.

2.8 Concluding Remarks

The literature reviews have shown that current plant design stages are not formally integrated with safety considerations and safety management programs are often carried out in series and towards the end of design stages. Conventional safety analysis tools including those reviewed in Section 2.1 are dependent of experience, influence and subjective inputs by team members. Manual data transfer from design into the analysis has resulted in their inability to quickly determine corresponding risk levels and consequence if process conditions are changed. Even the most commonly used technique, the QRA, cannot reflect this kind of changes efficiently because none of the present techniques are linked to a process simulator. Resulting from these shortcomings, safety features cannot be added proactively and hazards cannot be designed out proactively. Even though the application of Inherent Safety features is an attractive proposition to the industry as they are thought to be economically and technically viable, the lack of awareness, methodologies and tools have been identified, by previous researchers, as the barriers of applying inherent safety concepts to new designs.

In this research, a new framework is being developed to allow for risk of a particular design be assessed as early as the beginning of process simulation. This will allow design engineers to immediately analyze risk and consequence levels due to process conditions used in their simulation or design. This proposed framework can be accomplished by integrating the structured approach of QRA methodology into process simulator, which can provide process conditions in efficient manner. The integration can be built using Microsoft Excel, which is widely used and easily available. This is aimed to promote fast track adoption of the tool in the industry. Owing to the fact that risk is a function of consequence and probability, these two components will form part of the framework.

In order to materialize an integrated framework in which risk analysis can be carried out during process simulation stages, a prototype tool is developed based on HYSYS. This new tool is expected to allow users to create models quickly to evaluate many scenarios in new designs. The interactive environment allows for easy "what if" studies and sensitivity analysis. It also capitalizes on HYSYS's specialized thermodynamics packages for varieties of systems ranging from ideal to non-ideal conditions.

In order to provide design engineers an indication of the inherent safety level (ISL), an index module is required to be part of the proposed framework. In this present research, a two tier index system is being proposed. One to assess level of inherent safety at the level of process route selection (overall basis) while the other to assess inherent safety of respective streams for prioritization purposes. The indexing system has to be devised to overcome shortcoming of present indices as highlighted in Section 2.7.7 in order to quantify actual stream conditions by reflecting on the stream composition rather than taking them as individual components.

CHAPTER 3

Theories of Explosion

3.0 THEORIES OF EXPLOSION

CCPS (1994) defines an explosion as a release of energy that causes a blast which causes a transient change in the gas density, pressure and velocity of the air surrounding an explosion point. Similarly the Major Hazards Assessment Panel (1994) defines explosion as a process whereby a pressure wave is generated in air by a rapid release of energy. This definition encompasses widely differing events ranging from trivial example of a spark discharge through sudden release of stored energy in a compressed gas to the extreme of chemical detonations and nuclear explosions. The material involved in explosion is converted into a high-pressure gas at high temperatures and a rapidly expanding shock front. The pressure behind the explosion wave is the incident pressure. When the incident-pressure shock front strikes the front wall of the building, the pressure rises from ambient to the reflected pressure, which is a function of the incident pressure. A typical blast load is characterized by rapid rise in pressure to a peak value, a period of decay to ambient pressure (positive phase), and a period in which the pressure drops below ambient (negative phase). This is graphically represented in figure below.

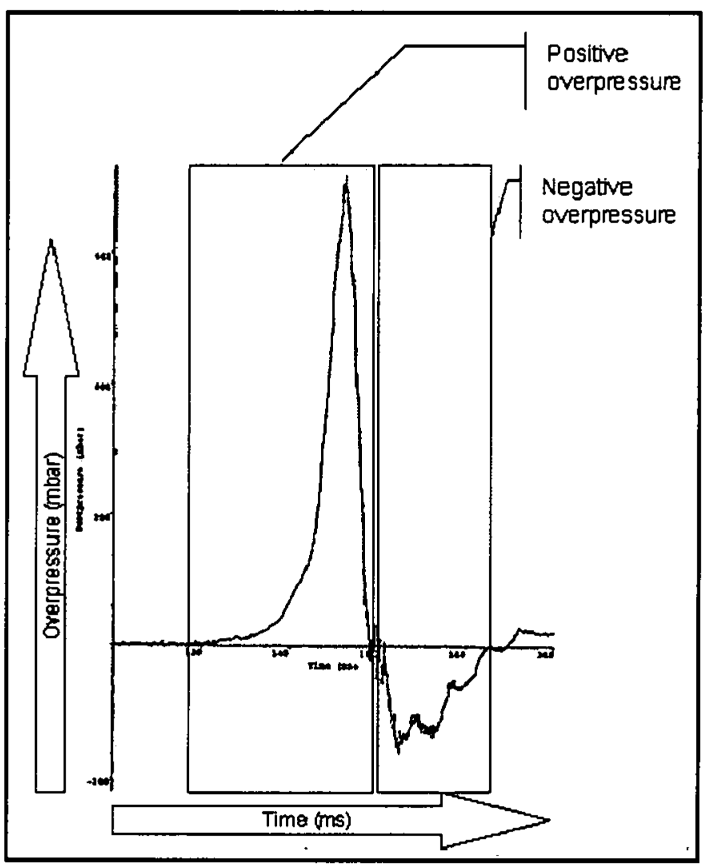


Figure 3.1 : Overpressure of an explosion (Philip Cleaver and Robinson, 1996)

The magnitude of the explosion effect (generally measured in pounds per square inch), which is very difficult to measure, reduces with distance from the center of the explosion. It is related in a more complicated way to the height of the explosion above ground level. For any given distance from the center of the explosion, an optimum burst height will produce the greatest overpressure. Conversely, an explosion on the surface produces the greatest overpressure at very close ranges.

Explosions in process plants typically occur due to the loss of containment of pressurized gas or pressurized boiling liquid, the rapid combustion of a flammable or finely divided solid material, or the uncontrolled reaction of chemical materials (API, 1995). Few known mechanisms of explosions are summarized in Table 3.1. Explosions can be classified as detonation or deflagration, depending on speed of the accelerating flame fronts. If flame front moves at or above speed of sound then the explosion is assumed as detonation otherwise it is a deflagration.

Table 3.1 : Types of explosion and characteristics

Types of Explosion	Characteristics
a. Vapor Cloud Explosion (VCE)	i. Result of a flame front propagating though a mixture of air and flammable gas or vapor. ii. The flame front must propagate with sufficient velocity to create a pressure wave
b. Boiling Liquid Expanding Vapor Explosion (BLEVE)	i. Result from the rapid release of a pressurized liquid above its atmospheric boiling point, usually caused by the rapid failure of its containment vessel. ii. BLEVE may produce an explosion wave, fragmentation, and, if flammable material is involved, a fireball.
c. Physical Explosion	i. Due to catastrophic failure pressurized system and resulting in release, which may cause VCE.
d. Chemical Explosion	i. Uncontrolled chemical reaction with sufficient energy may cause a failure of the vessel, resulting in overpressure and missile effects.

In most cases, indirect rather than direct pressure from a blast caused human injuries and deaths. While a human body can withstand up to 30 psi of simple overpressure, the winds associated with as little as 2 to 3 psi could be expected to blow people out of typical modern office buildings (American Petroleum Institute, 1995). Most blast deaths result from the collapse of occupied buildings, from people being blown into objects, or from buildings or smaller objects being blown onto or into people.

Vapor Cloud Explosion (VCE) is a term used to describe the explosive combustion of vapor and/or gas cloud formed by the release and then ignition of flammable materials. Vapor or gas cloud can be resulted from gas phase releases or evaporation from liquid phase. Due to heavier density of liquefied vapor, the possibility of forming clouds containing tons of vapor is much more higher than formation of gas clouds of huge masses. For a VCE to happen, several conditions have to co-exist. Flammable materials must be released and dispersed. Sufficient mixing with air (Oxygen) and presence of ignition source will cause combustion of the materials. Expanding volumes that is confined and faced with congestion will accelerate flame front. This will result in either deflagration or detonation as shown in Figure 3.2.

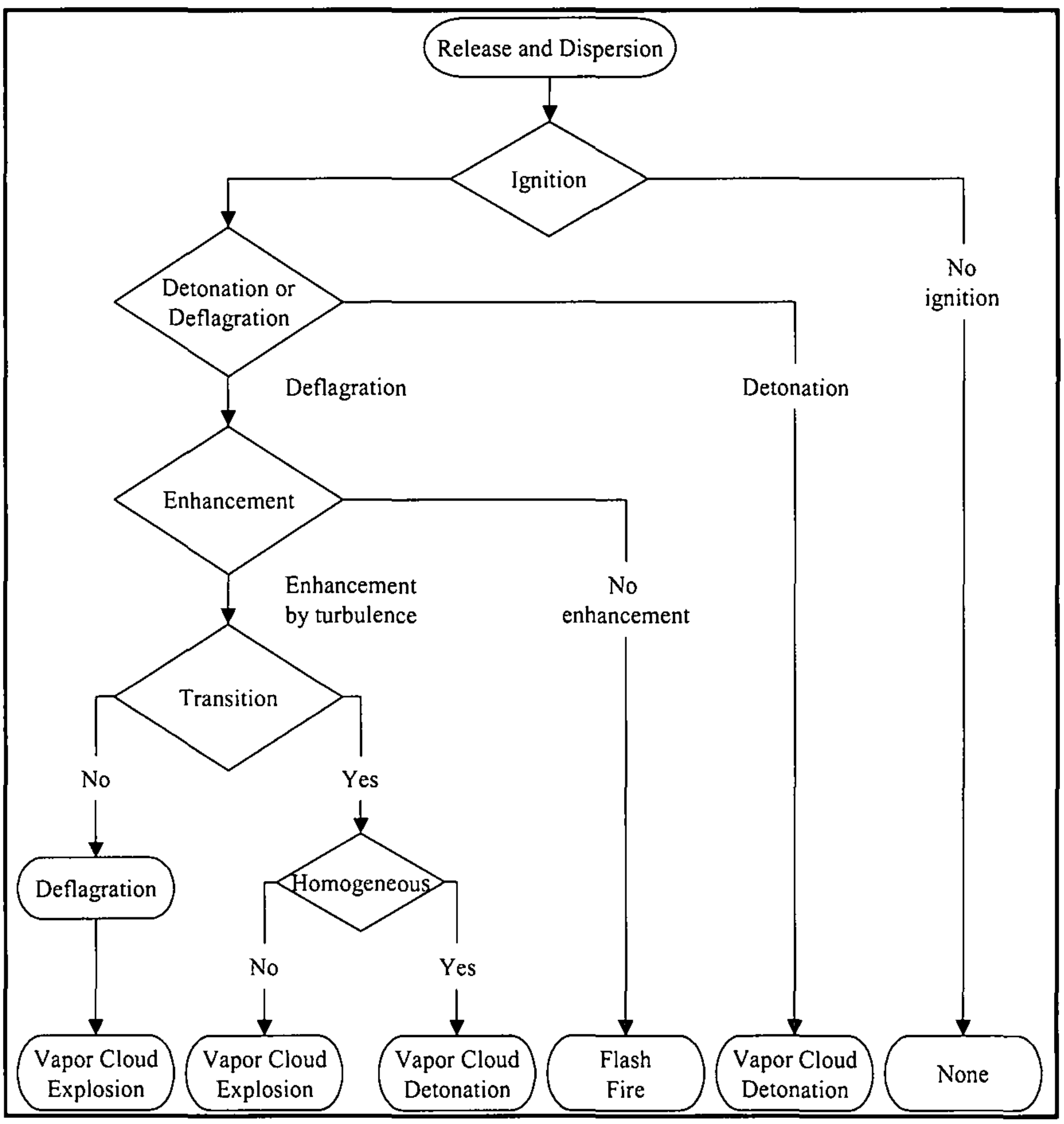


Figure 3.2 : Event Tree for VCE and flash fires (CCPS, 1994)

3.1 Releases of Flammable Materials

Total mass released in an accident can often be found by determining the inventory in the system before and after the release. However, this information is not sufficient to provide good estimates of flammable mass in the vapor cloud. This is because a release may consist of liquid (boiling or non-boiling), vapor or both phases. Therefore, it is preferable to calculate the discharge rates and concentration profiles. Calculations of these parameters require in-depth understanding of fluid flow characteristics. Details of such flow characteristics are described in literatures (Woodward, 1999) and (Munson et. al., 2002).

The Chemical Emergency Preparedness and Prevention Office (CEPPO), of the USEPA, (1999) recommended the assumption of sudden loss of containment to be the worst-case scenario. For substances in pipes, one must assume release of the largest amount in a pipe while for substances in vessels; one must assume release of the largest amount in a single vessel. The largest quantity should be determined taking into account administrative controls rather than absolute capacity of the vessel or pipe.

The prototype developed in this work can evaluate the amount of materials that would be leaked to environment if there has been a small-bore-hole leak on a pipe. The second scenario assumes a non-choked flow leakage while the third scenario assumes a choked flow. Choked flow usually occurs when the ratio of downstream to upstream pressure is in range of 0.5 to 0.9. Under choked flow conditions, the flow rate is insensitive to pressure variation downstream of the choked point. Discharge rates still depend on the pressure upstream of the choked point. In practice, liquid flow does not choke.

The present research work does not take into account for transition of choked flow regime to non-choked regime. The reason for this is because the simulation platform is HYSYS in Steady State mode, where time characteristics are not available. Furthermore, Figure 1.8 shows approximately 59% of the fire and explosion incidents happened during normal operations, implying steady state. Once the initial flow is choked flow, the calculation of mass being released will be based on that premise, when in actual situation, the flow may potentially change to non-choked

3.2 Flammability Limits and Heat of Combustion

Explosives can be classified as high, medium and low explosives. Higher energy explosives are like hydrogen and acetylene. Most hydrocarbons can be classified as medium explosives (Major Hazards Assessment Panel, 1994).

A flammable mixture can burn within a limit known as the flammable region, which is bounded, by Lower Flammability Limits (LFL) and Upper Flammability Limits (UFL). Please refer to Appendix C (page 136) for more information of flammability limits for various chemicals. If mixture of fuel is not between the boundaries, a VCE can be discounted. These limits are graphically represented in Figure 3.3.

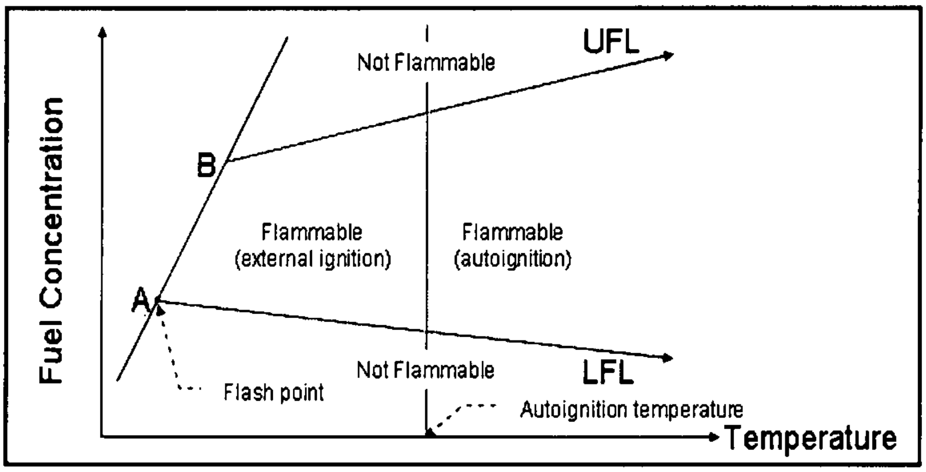


Figure 3.3 : Fuel Concentration – Temperature Diagram

Flammability limits for mixture can be estimated using the following equations (Wentz, 1999) which are based on the Le Chatelier's principle. Fraction in the vapor phase is used in the calculation of flammability limits for the mixture.

$$LFL_{mix} = \frac{1}{\sum_{i=1}^{n} \frac{y_i}{LFL_i}} \qquad \text{Equation 3-4}$$

$$UFL_{mix} = \frac{1}{\sum_{i=1}^{n} \frac{y_i}{UFL_i}} \qquad \text{Equation 3-5}$$

LFL_i = Lower Flammability Limit of component i

UFL_i = Upper Flammability Limit of component i

y_i = volume or mole fraction of component i in mixture

However, most of the flammability limits data are given at 25°C and atmospheric pressure. The flammability limits for individual components need to be corrected to the actual temperature and pressure before being used to determine the flammability limits of the mixture. The corrections can be carried out using equations below (Crowl D.A., Louvar J.F., 1990). The LFL is affected by temperature only while the UFL is influenced by pressure and temperature.

$$LFL_T = LFL_{25}\left[1 - \frac{0.75(T-25)}{\Delta H_c}\right] \quad \text{Equation 3-6}$$

$$UFL_T = UFL_{25}\left[1 + \frac{0.75(T-25)}{\Delta H_c}\right] \quad \text{Equation 3-7}$$

where
LFL_T = lower flammability limit at temperature, T (°C)
UFL_T = upper flammability limit at temperature, T (°C)
ΔH_c = heat of combustion for component, kcal/mol

The present research assumes all initial concentration of a release is above the C_{LFL} because it is the intention of the research to estimate Vapor Cloud Explosion, which could not happen if initial concentration is below C_{LFL}. If the initial concentration is above C_{UFL}, it is logical to assume that the concentration will fall within the flammability limits as time elapses.

Heat of combustion can be calculated using Equation 3-8 based on composition of the released materials CEPPO (1995). This is a used in cases where heat of combustion is not available in HYSYS databank.

$$HC_m = \frac{W_x}{W_m} \times HC_x + \frac{W_y}{W_m} \times HC_y \quad \text{Equation 3-8}$$

C_m = heat of combustion of mixture (kJ/kg)
HC_x = heat of combustion of component X (kJ/kg)
HC_y = heat of combustion of component Y (kJ/kg)
W_m = Weight of mixture (kg)
W_x = Weight of component X in mixture (kg)
W_y = Weight of component Y in mixture (kg)

3.3 Flammable mass fraction

Since the entire mass released will not be combusted, a mechanism to estimate flammable mass in an instantaneous point source Gaussian plume is included. This model is suitable because it is the simplest method, and applicable for use in preliminary assessment. Equations in this subsection are adopted from Woodward (1999).

The general equation for finding the flammable mass between the lower and upper flammability limits is a triple integral over the volume of the cloud between the coordinates at LFL, x_{LFL}, $\pm y_{LFL}$, $\pm z_{LFL}$:

$$m_f(t) = \int_0^{x_{LFL}} \int_{-y_{LFL}}^{y_{LFL}} \int_{-z_{LFL}}^{z_{LFL}} f(x,y,z,t)dxdydz \qquad \text{Equation 3-9}$$

where $f(x, y, z, t) = c(x, y, z, t)$ if $LFL<c(x, y, z, t)<UFL$

The concentration of $c(x, y, z, t)$ in kg/m^3 is expressed in terms of the discharge rate, w_p, the wind speed, u_w, and the lateral and vertical profiles by following equation for instantaneous (puff) source.

$$c(x, y, z, t) = w_p F_x(x, t) F_y(tu_w, y) F_z(tu_w, z) \qquad \text{Equation 3-10}$$

The cross-wind lateral dispersion for a point source is given in terms of σ_y which is a known function of distance x:

$$F_y(x,y) = \frac{1}{\sqrt{2\pi}\sigma_y(x)} \exp\left(\frac{y^2}{2\sigma_y^2(x)}\right) \qquad \text{Equation 3-11}$$

An analytical solution is available for the flammable mass in an instantaneous, point source Gaussian plume. Integration of Equation 3-10 using Equation 3-11 for either a grounded plume or a totally elevated plume between the LFL dimensions, $2x_{LFL}$, $2y_{LFL}$ and $2z_{LFL}$ gives the ratio of flammable mass to total mass in the cloud, m, as:

$$\frac{m_f}{m} = \text{erf}\left[\sqrt{\ln\left(\frac{C_o}{C_{LFL}}\right)}\right] - \text{erf}\left[\sqrt{\ln\left(\frac{C_o}{C_{UFL}}\right)}\right] - \frac{2C_{LFL}}{C_o\sqrt{\pi}}\sqrt{\ln\left(\frac{C_o}{C_{LFL}}\right)} + \frac{2C_{UFL}}{C_o\sqrt{\pi}}\sqrt{\ln\left(\frac{C_o}{C_{UFL}}\right)} \qquad \text{Equation 3-12}$$

C_{LFL} = Lower Flammability Limits of mixture

C_{UFL} = Upper Flammability Limits of mixture

C_o = Initial concentration of mixture

m_f = Flammable mass fraction

m = Mass released

when $C_o < C_{UFL}$ the equation above reduces to

$$\frac{m_f}{m} = \mathrm{erf}\left[\sqrt{\ln\left(\frac{C_o}{C_{LFL}}\right)}\right] - \frac{2C_{LFL}}{C_o\sqrt{\pi}}\sqrt{\ln\left(\frac{C_o}{C_{LFL}}\right)} \qquad \text{Equation 3-13}$$

Estimation of explosion mass is carried out by using Equation 3-13. If initial C_o is greater than C_{UFL}, the mixture would be out of the flammability limits and hence explosion is not possible at that point. However, it is also assumed that C_o will reduce and fall within flammability limits, thus presenting a possible explosive condition. The C_o has to be larger than C_{LFL} for the calculation to be valid.

In practice, neither failure location nor the prevailing physical conditions are accurately defined, so that the calculations of release rates cannot be carried out at great precision. Hence, it is acceptable that some simplifying assumptions are made which allow the necessary calculations to be performed manually (Woodward, 1999).

3.4 Dispersion of Flammable Mixture

Another important aspect in determination of Vapor Cloud Explosion is the dispersion or movement of the released flammable mixtures. Dispersion can increase or decrease flammable mass in the cloud. Dispersion, or equivalently air entrainment, according to the theory of atmospheric turbulence reviewed by Panofsky and Dutton (1984), is a process of mixing in which turbulent eddies of large wavelength eddies into eddies of ever smaller wavelengths. Dispersion is enhanced by a number of factors including jet mixing, surface roughness, wake effects, meteorology, averaging time and impingement.

Dispersion modeling requires numerous inputs especially with respect to meteorology and surface roughness. The models are often complicated multivariable integrals.

Since the present research will adopt a simplified approach to estimation in the preliminary stages, dispersion modeling is intentionally left out.

3.5 Ignition of Flammable Mixture

In the Chemical Process Industries, ignition sources are the only things can be observed in many situations (NFPA, 1991). Potential sources of ignition include open flames, electrical equipment, impact or friction and hot surfaces. Some materials can auto ignite. Since in most major incidents, the ignition sources cannot be identified, it is recommended to assume that sufficiently strong ignition sources are always present (Woodward, 1999; AIChE, 2000). This assumption is also adopted in the present research.

3.6 Congestion and Confinement

The explosion intensity of a VCE can vary greatly and is determined by the flame speed, which is in turn affected by the turbulence created within the vapor cloud. One of the key factors creating turbulence in a vapor cloud is the degree of congestion within the release area. Congestion is a measure of the amount and complexity of obstructions that may be encountered in the advancing path of a flame. Higher congestion results in higher turbulence of the vapor cloud. This in turn increases the flame front velocity and resulting in higher overpressure. Experience has shown that normal process plant design and equipment spacing may create enough congestion to cause turbulence and rapid flame propagation (API, 1995). A high-pressure jet release may also produce sufficient turbulence to increase the rate of flame propagation.

Confinement is a measure of the degree to which a cloud may be enclosed. The higher confinement will cause higher-pressure build up. This research focuses on application during earlier design stage when 3-dimensional layouts are not established, hence the influence of congestion and confinement are intentionally ignored.

3.7 TNO Multi Energy Correlation Method

This method was developed by the TNO Laboratory in The Netherlands by van den Berg (1985) and subsequently described in further detail by AIChE (1994). The TNO Multi-Energy method is increasingly accepted as a simple and practical method in estimating explosion blasts (Mercx et. el., 2000). The TNO method is based on interpretations of actual vapor cloud explosions incidents and assumes explosion as deflagration. This is due to the fact that detonation is more likely to be a resultant of high explosives rather than hydrocarbon fuels. TNO Multi Energy Method is able to estimate explosion parameters for most cases and it has been validated against actual incidents like Unconfined Vapor Cloud Explosion at Flixborough (Mercx et. al., 2000). The model further assumes that congestion has strong influence to the blast strength.

CCPS (2000) and Mercx et. al. (2000) provided guides on the steps involved in determining blast strength by calculating the peak overpressure resulting from an explosion. In this simple method, the blast from a vapor cloud explosion is modeled by the specification of an idealized explosive charge whose blast characteristics are available in the form of charts shown in Figure 3.4 and Figure 3.5. These charts have lines representing ten different blast strengths with line 1 being the weakest and 10 being the strongest. It is the view of AIChE (2000) that line 7 seems to be more accurately representing actual experience especially for hydrocarbon explosion. However the highest strength i.e. line 10, should be used in analysis where a detonation is to be assumed. This will lead to most conservative overpressure.

The Sachs scaled distance is a function of physical distance, explosion energy and ambient pressure. The Sachs scaled distance is calculated using:

$$\overline{R} = \frac{R}{\left(E/P_o\right)^{1/3}} \qquad \text{Equation 3-14}$$

where

$\overline{R}$ is the Sachs-scaled distance from charge (dimensionless)

R is the distance from charge (m)

E is the charge combustion energy (J)

P_o is the ambient pressure, (Pa)

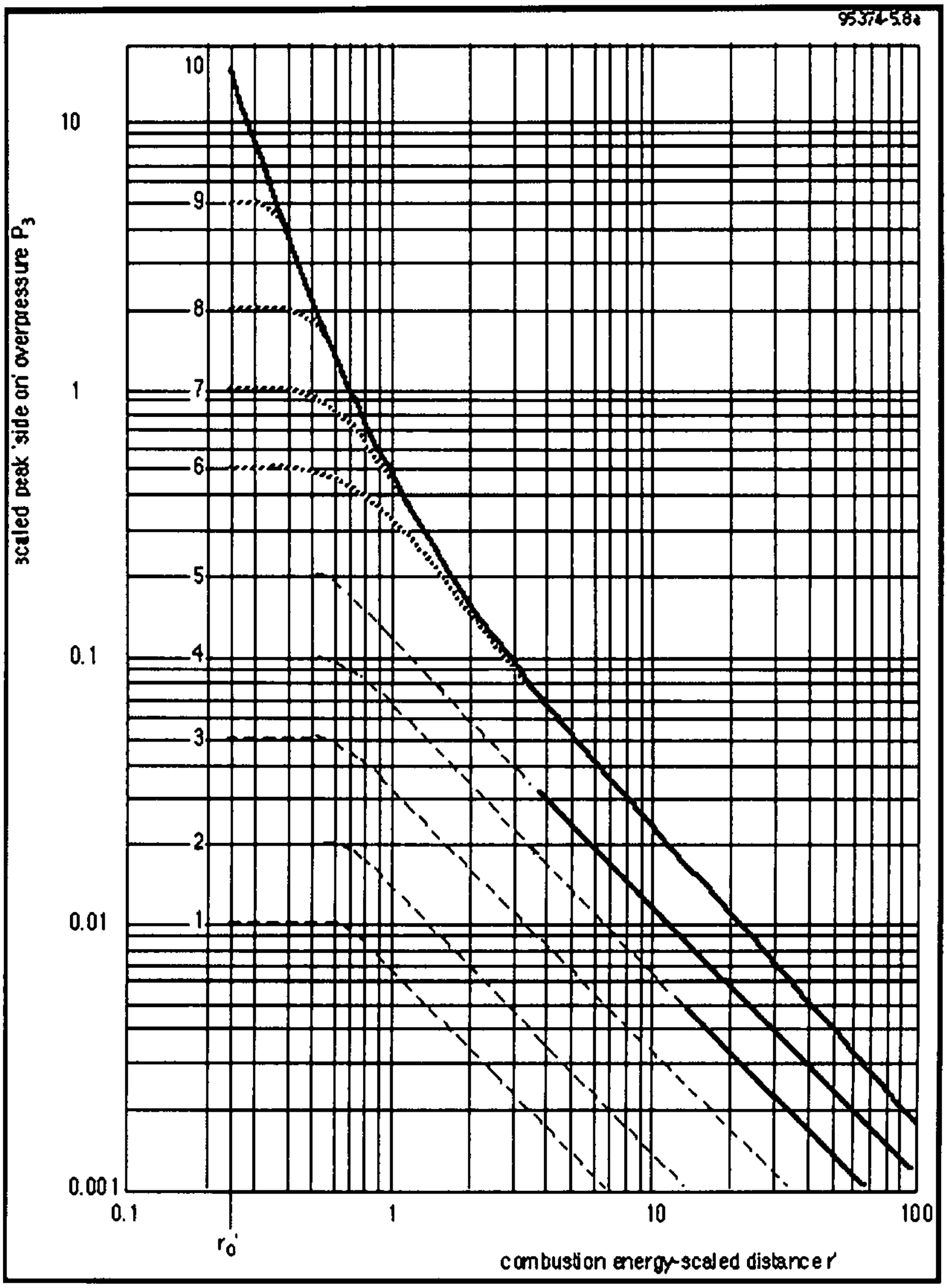


Figure 3.4 : Sach overpressure vs. scaled distance (CCPS, 1999)

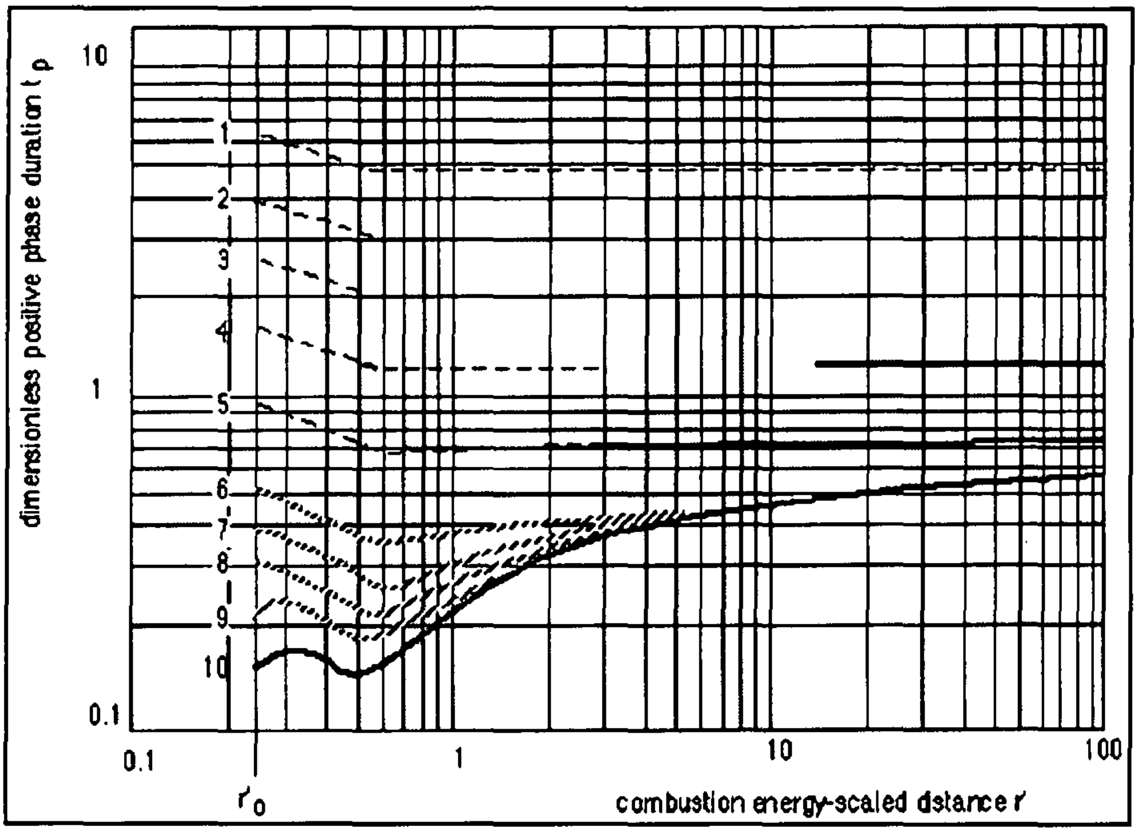


Figure 3.5 : Sachs dimensionless positive phase duration vs. scaled distance (CCPS, 1999)

3.7.1 Explosion Energy

According to the current TNO recommendations, the charge characteristics should be specified following a simple safe and conservative approach. The charge energy should be taken equal to the full heat of combustion of the flammable mixture present within the area of turbulence generative boundary conditions in the cloud, assuming that the fuel is stoichiometrically mixed with air. Charge energy can be calculated as:

$$E = \Delta H_{comb} \times m_f \qquad \text{Equation 3-15}$$

where

E is the charge combustion energy (J)

ΔH_{comb} is the combustion energy, (J/kg)

m_f is the explosive mass calculated from Equation 3-13

3.7.2 Sachs Side On Over Pressure Calculations

By using substituting Equation 3-15 into Equation 3-14 and then using the appropriate charge strength line in Figure 3.4, the Sachs scaled side on blast overpressure can be determined. The charge strength should be assumed to be maximum i.e. 10 in Figure 3.4 (Mercx et. al., 2000) to obtain conservative results. Other literatures recommend that a strength of 7 to be used in hydrocarbon explosion.

The Sachs-scaled side-on overpressure is related to the actual side-on overpressure by

$$P_s = \Delta\overline{P}_s \times P_o \qquad \text{Equation 3-16}$$

where

P_s is side-on blast overpressure (Pa)

$\Delta\overline{P}_s$ is the Sachs-scaled side-on overpressure (dimensionless)

P_o is the ambient pressure (Pa)

In order to program the blast curves into computer software or spreadsheet, AIChE (2000) produced the data sets by digitalizing Figure 3.4. These data sets are attached in Appendix D. The present research developed a mathematical model to describe these curves by using non-linear regression technique. By using non-linear regression software (Curve Expert 1.3), the rational function is recommended as a model for the 10 curves. The generic rational function is given as

$$\Delta\overline{P}_s = \frac{\left(a + b\overline{R}\right)}{\left(1 + c\overline{R} + d\overline{R}^2\right)} \qquad \text{Equation 3-17}$$

Where

$\Delta\overline{P}_s$ = Sachs-scaled side-on overpressure

$\overline{R}$ = Sachs-scaled distance

a, b, c, d = coefficients which depends on blast strength

The coefficients for equation above are generated using non-linear regression software and provided in Table 3.2. As an illustration, if user decides to use curve 7, then by substituting the coefficients from Table 3.2 for curve 7 into Equation 3-17 gives

$$\Delta\overline{P}_s = \frac{(0.6354 + 0.4462\overline{R})}{(1 - 1.7095\overline{R} + 2.9456\overline{R}^2)} \qquad \text{Equation 3-18}$$

$\Delta\overline{P}_s$ = Sachs-scaled side-on overpressure

$\overline{R}$ = Sachs-scaled distance

Table 3.2 : Coefficients for blast curve equations

Blast Curve	Coefficients			
	a =	*b* =	*c* =	*d* =
1	0.0060	0.0130	-0.7543	2.4012
2	0.0120	0.0276	-0.7051	2.4420
3	0.0255	0.0945	-0.7947	3.3844
4	0.0587	0.1583	-0.6573	2.7745
5	0.0857	0.4219	-1.0401	4.0692
6	0.3719	0.3957	-0.6480	1.9536
7	0.6354	0.4462	-1.7095	2.9456
8	0.8943	0.3514	-2.9947	4.3123
9	0.3486	2.5534	-5.5645	9.7871
10	4.49E+10	-1.09E+10	-1.07E+10	8.40E+10

In order to ascertain that the Sachs-scaled side-on overpressure calculated by using Equation 3-7 matches the original data set provided by AIChE, test of correlation coefficient is conducted for all the blast curves. The correlation coefficient is a measure of how well trends in the predicted values follow trends in the actual values. It is a measure of how well the predicted values from a forecast model "fit" with the given data set. The correlation coefficient is a number between 0 and 1. If there is no relationship between the predicted values and the given values the correlation coefficient is 0 or very low. As the strength of the relationship between the predicted values and actual values increases so does the correlation coefficient. A perfect fit gives a coefficient of 1.0. Thus in this instance, the higher the correlation coefficient the better the model i.e. Equation 3-7 and its respective coefficients in mirroring the data set by AIChE. Results of the analysis (by using Excel spreadsheet functions) are provided here:

Table 3.3 : TNO blast curves data and calculated data correlation coefficients

Blast curve 1	0.9984
Blast curve 2	0.9985
Blast curve 3	0.9993
Blast curve 4	0.9997
Blast curve 5	0.9994

Blast curve 6	0.9999
Blast curve 7	0.9998
Blast curve 8	0.9985
Blast curve 9	0.9984
Blast curve 10	0.9997

The correlation coefficients are all greater than 0.99, at such it can be concluded that Equation 3-7 and the coefficients in Table 3.2 matches the given data sets in Appendix D. The equation and the coefficients are subsequently adopted into the research.

3.8 Determination of Damages and Injuries

Explosions cause damages to properties as well as injuries and/or death to human due to the generation of overpressure. Major agencies and researches have quantified or correlate damages observed in explosion incidents to overpressure measured. Information on the effects of air blast on a wide variety of objects has been given by Glasstone and Dolan in 1977. These include buildings of various kinds, gas works, LPG installation and sewage system. His database was fundamentally based on damages caused in Hiroshima and Nagasaki by the explosions of nuclear bombs of approximately 20000 ton of TNT. Data from a report by Clancey (1972) on the effects of a blast is provided in Appendix G of this thesis for reference. More recent data of actual cases of explosions such as the Flixborough and St. Herblain accidents are also available in the public domain.

The Netherlands Organization (TNO) of Applied Scientific Research (1989) published a guideline and recommends the use of the following equation for the determination of possible damage to people and objects resulting from explosions.

$$R_i = C_i\left(\eta M E_c\right)^{\frac{1}{3}}$$
$$\eta = \eta_c \eta_m$$
Equation 3-19

R_i = Maximum distance within which certain damage can be expected

C_i = Constant for application of TNO correlation model.

η_c = Efficiency factor = 0.30

η_m = Mechanical efficiency = 0.33.

M = Total mass of flammable material in the cloud (kg)

E_c = Lower heat of combustion (kJ/kg)

Parameters and constants used in this equation are recommended by Wiekema (1979), who also proposed this method of estimating explosion energies for medium explosives like ethane, propane, butane and cyclohexane. To determine maximum distance where "significant damage to buildings and process equipment" can be observed, use C_i = 0.03. Maximum distance to where repairable damage to buildings and damage to house façade, use C_i = 0.06. C_i = 0.15 is used to calculate maximum distance to places where breakage of glasses and injuries are observed while 0.40 is for maximum distance to threshold of glass breakage (10% of total).

3.8.1 Probit Functions

Another mean of quantifying damage and injuries resulting from overpressure is by the use of probit function. Probit (probability) function provides a transformation method to convert the dose-response curve shown in Figure 3.6, into a straight line. The dose-response curve is a sigmoidal-shaped curve which describes cumulative response to a particular dosage of hazard (in logarithmic axis). The probit relationship to percentage is described by CCPS (2000) via the following equation

$$P = \frac{1}{\sqrt{(2\pi)}} \int_{-\infty}^{P_r - 5} \exp\left(\frac{-u^2}{2}\right) du \qquad \text{Equation 3-20}$$

Where

P_r = probit variable, which depends on type of hazard, damage and injuries

P = probability or percentage

u = integral variable

For spreadsheet computations, a more useful form of the above equation is used in calculations for this research work and is presented as

$$P = 50\left[1 + \frac{P_r - 5}{|P_r - 5|} \operatorname{erf}\left(\frac{|P_r - 5|}{\sqrt{2}}\right)\right] \qquad \text{Equation 3-21}$$

Where

P_r = probit variable, which depends on type of hazard, damage and injuries

P = probability or percentage

erf = error function (computed within spreadsheet)

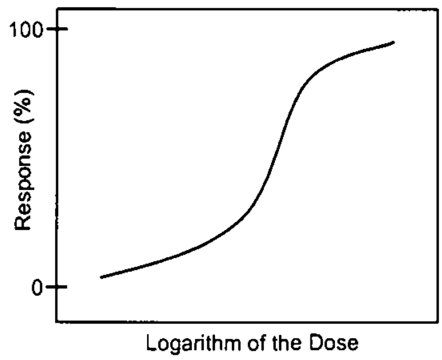


Figure 3.6 : Typical response versus log (dose) curve

The probit variable, P_r, in Equation 3-21 for explosion has the following generic form

$$P_r = a + b.\ln(P_s) \qquad \text{Equation 3-22}$$

P_r = probit variable
a, b = constants
P_s = overpressure from Equation 3-16

The constants are derived from analysis of actual damage observed and experiments by using curve fitting techniques. Salzano and Cozzani (2005) along with TNO (1989) provided the constants for several cases.

Table 3.4 : Probit equation constants (Salzano and Cozzani, 2005; TNO, 1989)

Case	**Constant for Equation 3-22**	
	a	**b**
Structural damage due to overpressure	-23.8	2.92
Glass breakage due to overpressure	-18.1	2.79
Death from lung hemorrhage due to overpressure	-77.1	6.91
Eardrum rupture due to overpressure	-15.6	1.93
Damage to atmospheric vessels due to overpressure	-18.96	2.44
Damage to pressurized vessels due to overpressure	-42.44	4.33
Damage to elongated vessels due to overpressure	-28.07	3.16
Damage to small equipment due to overpressure	-17.79	2.18

3.9 Calculating Probability of Explosion

Based on the literature presented in Section 2.4, the present research derived an equation to describe its probability properties based on original data compiled from various sources by Withers (1988). Similar to the work in Section 3.7.2, a non-linear regression software was used to produce the following equation

$$P_{ex} = 0.0175 \times \left(0.9999^{m_f}\right) \times \left(m_f\right)^{0.4582} \qquad \text{Equation 3-23}$$

Where
P_{ex} = probability of explosion
m_f = mass of combustible from Equation 3-13

Equation 3-23 is validated with the original data (center column) by Withers (1988) and tabulated as comparison as follows in Table 3.5 below. The correlation coefficient between the calculated data and the given data is 0.9988, signifying a good match. The same data is plotted in Figure 3.7.

Table 3.5 : Validating equation for probability of ignition and explosion

Release size (tons)	**Chances of ignition & explosion (Withers, 1988)**	**Calculated data**
5000	0.7	0.694994
2000	0.5	0.522026
1000	0.4	0.397292
500	0.32	0.295702
200	0.2	0.196936
100	0.15	0.143989
50	0.11	0.105043
20	0.06	0.069121
10	0.04	0.050336
5	0.025	0.036647
2	0.012	0.024086
1	0.006	0.017533
0.5	0.003	0.012762
0.2	0.001	0.008387
0.1	0	0.006105

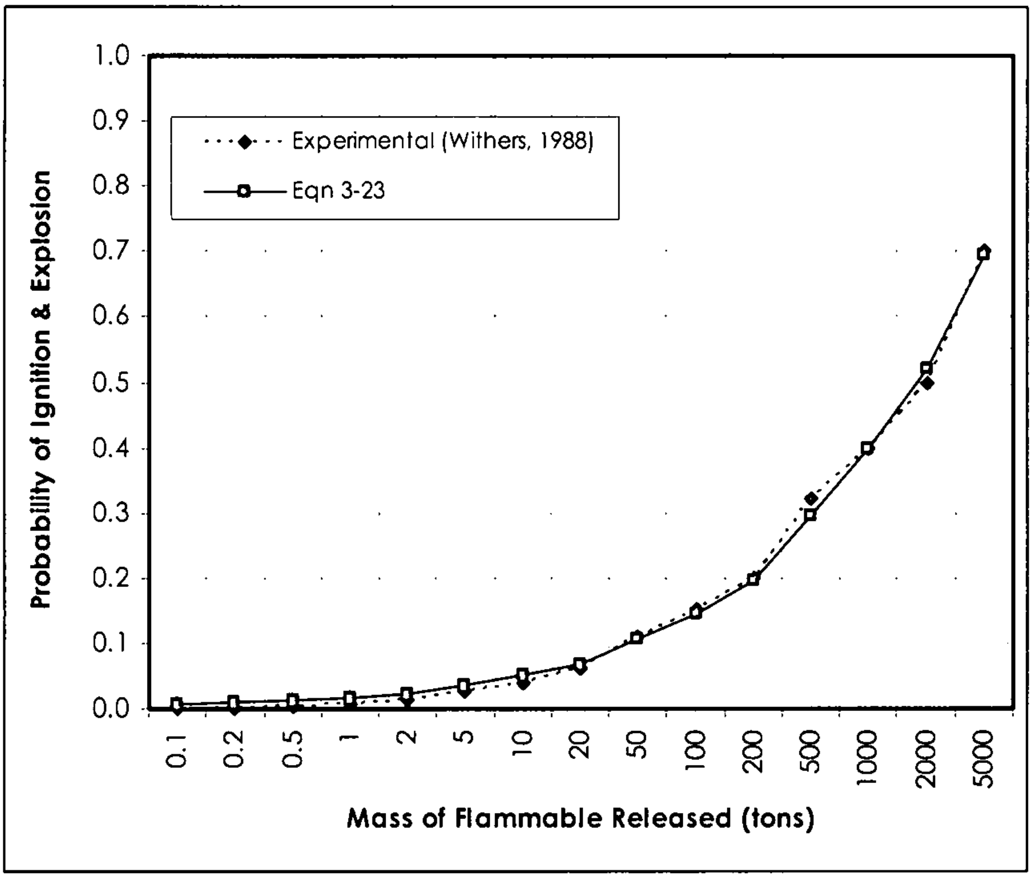


Figure 3.7 : Probability of ignition and explosion

CHAPTER 4

Inherent Safety Intervention Framework

4.0 INHERENT SAFETY INTERVENTION FRAMEWORK

The chemical process industry focuses particularly at energy, capital expenditure and variable feedstock cost savings due to fierce global competition, the Kyoto Protocol and requirements for sustainable development. Attention to safety is often given to adequately ensure that risks from the plant are as low as reasonably practicable (ALARP). This is achieved often through the additional damage control and mitigation measures rather than reduction or elimination of the original hazards. Examples of safety protection devices include barriers such as pressure relief valves and instrumented protection functions (IPF). However, it is important to bear in mind that these devices themselves require expensive maintenance (Lutz, 1997) and they can suffer partial or complete dangerous failures (undetected failure). In cases on undetected failures, the original hazards are still present, and accidents can still occur and the consequences could be worsened by generous-failure mode of the barrier.

A feasible alternative is to reduce or eliminate the original hazard while the plant is being designed. This can be achieved by adopting the principles of Inherent Safety proposed and formalized by Kletz (1991) into stages of chemical process plant design. The earlier these principles are applied to the design stage, the more cost effective it is because any redesign in later stages would naturally take more man-hours and cost. Section 2.6 of this thesis has discussed this in greater detail.

Even though the concept of Inherent Safety had been proposed for more than a decade, the concept is still lacking wide application in the process industry mainly due to implementation constraints described in Section 2.6.1. Further to that, Hendershot (2002) noted that many inherently safer options could be available for a particular case but their applications are hindered due to unavailability of systematic analytical methodology in this area. In order to address these issues, and for the principles of Inherent Safety to be applied appropriately, a method to quantify and represent the inherent safety of a particular process route during early stages of process design is being proposed in this research.

This present research adopts the structured thought processes of a typical QRA and combining it with concept of inherent safety which is to proactively reduce risk relating to a particular process being designed. The resultant framework is expected to provide an indicative risk of a process by means of estimating the consequences and probability of an undesired event during preliminary design stage and addressing critical issues relating to quantification of ISL as described in Section 2.7.7. This new framework is defined by this research as the Inherent Safety Intervention Framework (ISIF). ISIF can be developed to estimate risk and consequences of various hazards including fire, explosion and toxic release. However in present research the ISIF is being illustrated by focusing on explosion hazard as this hazard had in the past resulted in the highest amount of monetary losses (Figure 1.6).

For ISIF to deliver the expected results in providing necessary risk indication during early process design stage, it is crucial for the right critical information to be provided to the estimation mechanisms at the earliest opportune juncture. Critical process information or parameters often required in estimating the consequences are pressure, temperature and composition of the fluid being processed or stored. Process information mentioned above is readily available via process simulators and in the present research ISIF is integrated with HYSYS for seamless process data transfer. By integrating process parameters directly into calculations, risk relating to changes in simulation conditions can be efficiently re-estimated as required. Physical and chemical properties such as density, heat of combustions etc. of the fluids are important factors as well. These properties are readily available in Chemical Safety Data Sheets (CSDS) or Material Safety Data Sheets (MSDS). For the purpose of the present research, physical and chemical properties for 120 types of chemicals have been included in a database for reference by the formula described in Chapter 3.0. These 120 types of chemicals include common hydrocarbons and petrochemicals which are subsequently used in the cases in Chapter 5.0. The probability component of risk is calculated based on typical explosion described by the Event Tree Analysis (ETA) in Figure 4.5 and used in conjunction with failure rates which are available in the database of the ISIF prototype.

Referring to Figure 1.2, the earliest possible and most viable juncture for the integration is when process routes are being selected as simulation tools are expected to come into first use. This is illustrated in Figure 4.1. This integration allows designers to identify a process route that uses inherently safer process conditions, chemical along with traditional considerations like cost and efficiency. Through initial simulation, process data will be available and changes can be easily made. Mohd. Shariff et. al. (2006) presented a similar concept which utilized process data from initial simulation to determine possible consequences from explosion and subsequently determine the minimum distance required from a potential hazard.

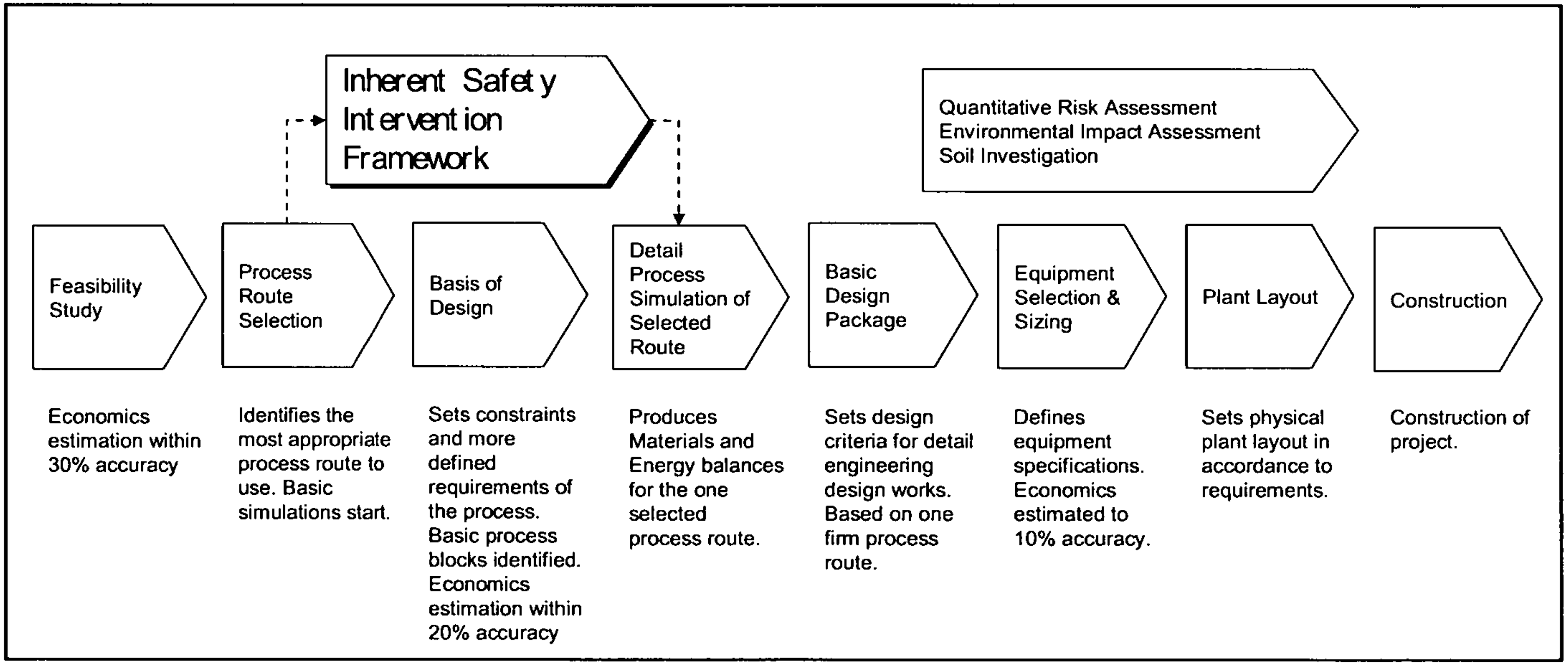


Figure 4.1 : Integration of Inherent Safety Intervention Framework (ISIF) with process design stages

Having noted the required mechanisms to make up the ISIF, an algorithm or sequence is developed to obtain the optimum and practical result. The ISIF is designed on the basis that it would be used to select the inherently safer route from various routes that can be used to produce the same product and that the same tool can then be used to assist improvement efforts within the selected route. This is illustrated in Figure 4.2. Explosion hazard has been chosen as model in the development of this framework because this hazard, as established in Figure 1.6 and Figure 1.7, is the most common in the chemical process industries and had caused the largest monetary losses. At such, the screening methods and inherent risks are calculated to reflect explosion hazard of the processes.

This algorithm is further translated into computer software tool based on Microsoft Excel spreadsheet to capitalize on its calculation ability and its Visual Basic for Application (VBA) language which can be used to communicate with process simulator, HYSYS as described at the end of Section 1.1.2. Human intervention is still required for making decision on whether to proceed with additional improvement or otherwise. On the same token, human ingenuity is indispensable in the process modification efforts, which can be based on the Inherent Safety Principles. It is important to note that whatever modifications carried out to enhance the level of Inherent Safety should not in anyway impair the original design intent and product specifications.

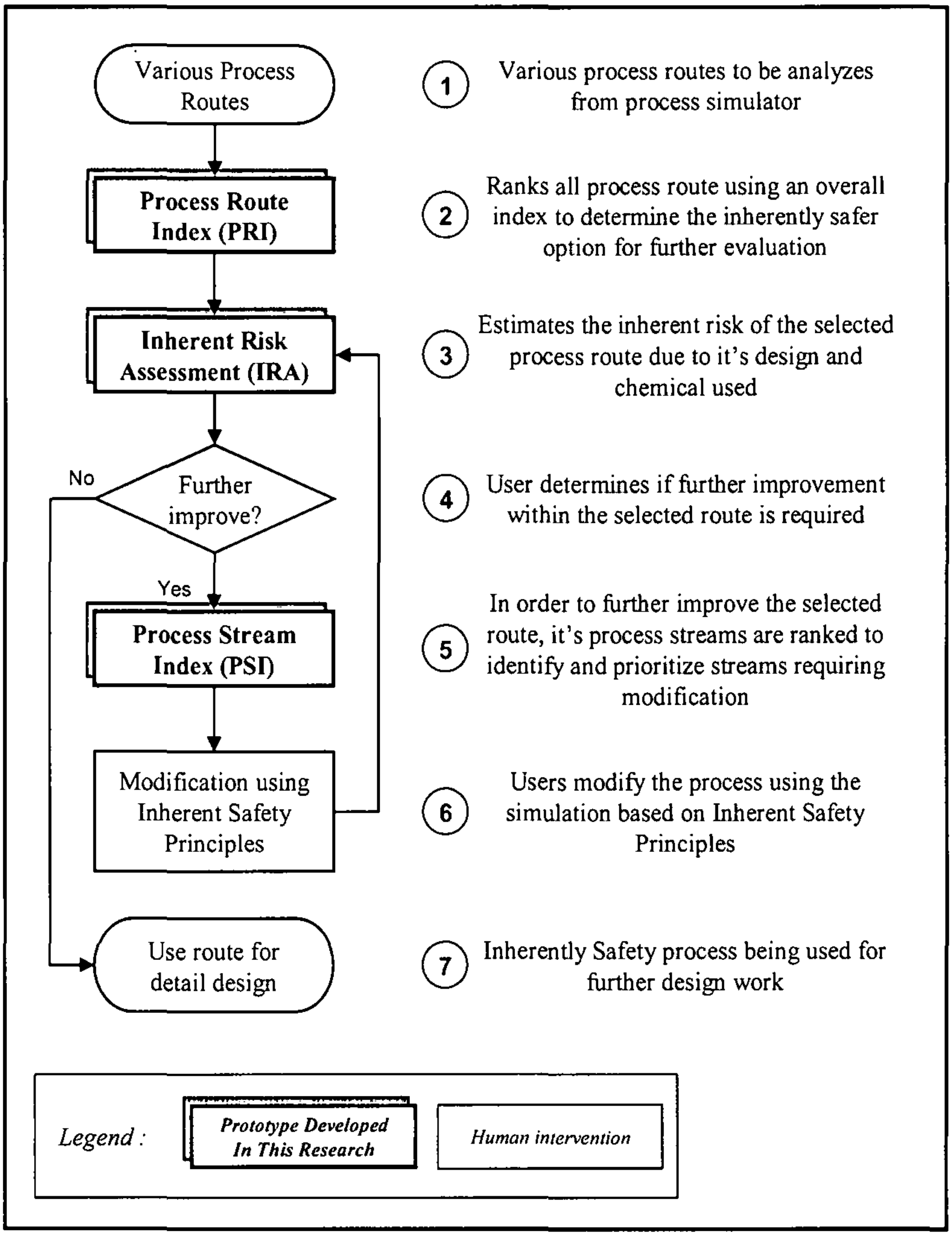


Figure 4.2 : Inherent Safety intervention algorithm

This research developed the modules to perform the tasks of process routes screening, inherent risk assessment and process stream prioritization illustrated in shaded box in Figure 4.2 and are further deliberated in the following sections of the thesis.

Process data such as temperature, pressure, density, composition are provided from HYSYS to Excel in tabulated format. The VBA codes are used to perform this task and are embedded within the spreadsheet and are programmed using some library functions specifically developed by HYSYS software. This set of data is passed to the module which screens the process routes by evaluating their relative ranking based on

Inherent Safety Index method to be discussed in Section 4.1. Inherent risk is estimated for the selected process route. In the present prototype, the calculations provides the inherent risk due to explosion since explosion hazards had caused the most damage in the chemical process industries (Figure 1.6) and also the most predominant type of event (Figure 1.7) historically. The last module provides the design engineer a means to rank and then identify the stream which has higher inherent risk by means of another index that is described in Section 4.1.

The estimation techniques used in the modules have been adequately described in Sections 2.4, 3.8 and 3.9. Inherent risk is presented by using similar means as an FN curve. Since this framework is meant to provide indicative risk inherent to the design in the early stages and not as final QRA for safety cases, the numerical limits as described in Section 2.3 and illustrated in Figure 2.7 are not used. Instead the FN curve for IRA as only two regions and this is further deliberated in Section Inherent Risk Assessment **(IRA)**4.2.

The ISIF is likely to be able to address the gap preventing wide application of Inherent Safety in the industries as highlighted in Section 2.6 by Kletz (1991), Rushton et al. (1994), Mansfield, Kletz and Al-Hassan (1996) and the latest survey findings by Gupta and Edwards (2002). The research hypothesize that inherently safer process designs can be produced by applying ISIF to identify and quantify inherent risk and subsequent intervention to reduce the hazard from early design stages. The modifications to improve the level of inherent safety of a process can be based on the relevant principles of Inherent Safety as presented in Table 2.11.

By using the ISIF which is integrated with process design software, in this case HYSYS, design engineers can contemplate more scenario or process routes by using without compromising data accuracy and without significant cost.

4.1 Two Tiered Inherent Safety Indices (2t-ISI)

An efficient indexing method is required for process route screening and process stream prioritization as shown in Figure 4.2. The present research conducted a literature review to understand the available indices and concluded that the present inherent safety indices described in Section 2.7 have the following limitations:

1. no single representative number to present overall inherent safety level of a process route
2. there is a lack of sub index or parameter interaction to reflect actual process stream condition
3. range scoring methodology would not be able to differentiate between parameters that fall within the same range
4. the industry felt that too much manual transfer of information can be cumbersome for application in the early development stages and a quicker method is required (Gupta and Edwards, 2003)

In order to address these shortcomings, the present research proposed a two tier Inherent Safety Index Module (2t-ISI). The fundamental principles for the index and integration with process design software has been discussed by Chan and Mohd. Shariff (2008). The first tier known as the Process Route Index (PRI) is to be used for relative ranking of process routes while the second tier is the Process Stream Index (PSI), which quantifies the inherent safety levels of individual process streams within the selected design. Both the PRI and PSI are developed using parameters that account for actual conditions of the streams to address the concerns illustrated in Section 2.7.7 and Table 2.18. The 2t-ISI extracts information directly from process simulator i.e. HYSYS and quantifies the level of Inherent Safety. Information such as chemicals, process conditions and inventory is quickly available in the simulation. The 2t-ISI can be reevaluated for every process condition change in the simulation at very little cost and very little time. Application of the 2t-ISI is illustrated in Figure 4.2 as step 2 and step 5.

Results from PRI and PSI are used to relatively rank and evaluation options. Examples are provided in following sections to further illustrate this concept, which has been introduced earlier in Section 2.1.6.

4.1.1 Process Route Index (PRI)

The philosophy for the new index is based on fundamental process parameters that influence the outcome of an incident. With reference to Equation 3-19, it is noted that in the case of explosion, the process parameters that influence consequences include mass released, M and energy, E_c. The notation C_i and η in the equation are non process related empirical constants. The present research is in the view that combustibility (difference between UFL and LFL) of the process chemical needs to be considered. This view is similar to Lawrence (1996) who proposed the PIIS and Heikkilä (1999) who proposed the ISI. The larger difference between UFL and LFL for a given substance or mixture implies that the chances of ignition is higher. This has been illustrated in Figure 3.3 where a larger area (flammable region) can be expected as the difference between UFL and LFL increases. Following this, the PRI is a function of mass, energy and combustibility as described by Equation 4-1.

$$\text{PRI} = f(\text{mass, energy, combustibility}) \qquad \text{Equation 4-1}$$

In order to use data from process simulator for calculation, the term "mass" in Equation 4-1 has to be converted into basic process parameters. Using principles of fluid mechanic, amount of mass flowing through a hole (in the case of a leak) is a function of density and pressure differential between system and the surrounding. Substituting density and pressure into Equation 4-1 yields Equation 4-2

$$\text{PRI} = f(\text{density, pressure, energy, combustibility}) \qquad \text{Equation 4-2}$$

The combustibility (ΔFL_{mix}) is determined as the difference in flammability limits, which have been corrected for effects of process temperature and pressure using Equation 3-6 and Equation 3-7.

Since the PRI is to represent the overall process route, the present research propose the PRI to use the averages of the properties in Equation 4-2 and resulting in Equation 4-3

PRI = [(average mass heating value) x (average fluid density) x (average pressure) x (average ΔFL_{mix})] $\div 10^8$ Equation 4-3

The parameters in Equation 4-3 can be obtained directly from process simulator, HYSYS. A simple average of the respective parameter is calculated considering all the streams to determine the average value of the parameter for the particular process route. The averages are then multiplied and divided by an empirical constant, 10^8. The division by 10^8 serves to reduce the magnitude of the resulting numbers in order for them to be easily comprehensible. However it is important to note that this particular constant is only applicable for the 120 chemicals available in the present prototype and may need to be adjusted when other chemicals are considered. Based on the principles used to derive Equation 4-3, it can be inferred that larger PRI value indicates the route is inherently less safe from explosion perspective compared to a route having smaller PRI value. A sample calculation based on data provided in Appendix H is results in the PRI for this route as 0.45.

Average mass heating value = 11195.19 Average ΔFL_{mix} = 9.74

Average stream density = 49.97 Average pressure = 8.33

PRI = 11195.19 x 49.97 x 9.74 x 8.33 $\div 10^8$
= 0.45

The PRI for the individual routes can be calculated and used as a numerical representation of the routes. These numbers are relatively ranked and provide an indication as to which route is inherently safer. Extending the sample calculation above to 4 different process routes that produce methyl methacrylate (MMA), the following PRIs are obtained. These four different process routes were based on initial work by Lawrence (1996).

Table 4.1 : Relative Ranking of PRIs for four MMA production routes

Methyl Methacrylate (MMA) Process Routes	**Process Route Index (PRI)**	**Relative Rank**
Ethylene via methyl propionate based route (C2/MP)	76.5	4
Ethylene via propionaldehyde based route (C2/PA)	32.3	3
Isobutylene based route (i-C4)	9.1	2
Tertiary Butyl Alcohol based route (TBA)	3.3	1

By adopting the relative ranking approach, the PRIs clearly show that TBA route ranks first in terms of inherent safety, from perspective of explosion, while the C2/PA route is last. This hypothesis is validated against previous research findings by Lawrence (1996), Heikkilä (1999) and Palaniappan (2002) in Chapter 5.0.

4.1.2 Process Stream Index (PSI)

From the assessment of individual parameters using Heikkilä (1999) index as demonstrated in Table 4.2, it is impossible to tell which particular stream will cause more damage if there is a loss of containment and subsequently causing an explosion. Looking at the temperature perspective, stream S is the "most dangerous" among them as it has the highest index due to higher temperature. When the pressure parameter is considered, streams R and U have the same index while stream S is deemed to be the most dangerous. The same can be concluded for PIIS and i-Safe as well.

Table 4.2 : Assessment of streams using traditional IS indices

	Traditional inherent safety indices					
	Temperature		Pressure		Δ(UFL-LFL)	
Stream	°C	Index	kPa	Index	%	Index
R (feed to R100)	130	2	200	1	23.59	3
S (hp air)	235	3	500	2	0	0
U (Propylene)	40	1	200	1	7.50	2

In Heikkilä's original work, she used the difference between Upper Flammability Limit (UFL) with the Lower Flammability Limit (LFL) as a measure to represent the easiness of combustion and explosion. The larger the difference, the easier it would be for combustion to occur. When this index is referred in Table 4.2, stream R is determined to be most dangerous among the three streams. This example shows the complexity of determining the most dangerous stream. This can be more complex when the whole flow sheet is being considered instead of just three. Similar shortcoming can be expected if other indices described in Section 2.7.1 to Section 2.7.6 are applied to the same situation as they are all treat each parameter individually and use fixed scale.

In order to address the shortcoming demonstrated above, the second tier of the 2t-ISI is developed by improving and adopting similar approach as in Section 4.1.1. The new index known as the Process Stream Index (PSI) can be used to rank stream ISL which can be the basis to channel modification efforts to particular stream in order to design inherently safer process. The PSI also addresses another disadvantage of previous indices, which are focused only on assessing the reactions and thus only able to differentiate ISL of process routes. The PSI adopts the same theoretical foundation as Equation 4-2 and uses process information which is available from process simulator and does not involve complicated calculation.

In order for sensible comparison between one stream to another stream, for a particular property e.g. heating value, each stream is gauged against the average value of that property within the simulation. The result is a relative ranking or relative position of the stream within all the streams in a simulation. An illustration is provided here using the heating value for a simulation case containing 33 streams. The simulation is for production of acrylic acid via propylene oxidation. The average heating value for these 33 streams listed in Table 4.3, is computed to be 12793kJ/kg and the distribution of heating values is shown in scatter plot in Figure 4.3.

Table 4.3 : Heating values for 33 process streams within a simulation

Stream	Heating Value	Stream	Heating Value	Stream	Heating Value
A	17764.61	L	35000.27	W	18568.02
B	17655.98	M	36118.38	X	16868.82
C	0.00	N	17745.83	Y	0.00
D	0.00	O	0.00	Z	18568.02
E	0.00	P	36154.92	AA	16868.82
F	14300.89	Q	36234.57	AB	16957.00
G	6432.23	R	18568.02	AC	6788.05
H	153.62	S	0.00	AD	6432.23
I	5466.70	T	6788.05	AE	18568.02
J	5363.02	U	45831.34	AF	52.40
K	2868.96	V	0.00	AG	36.15

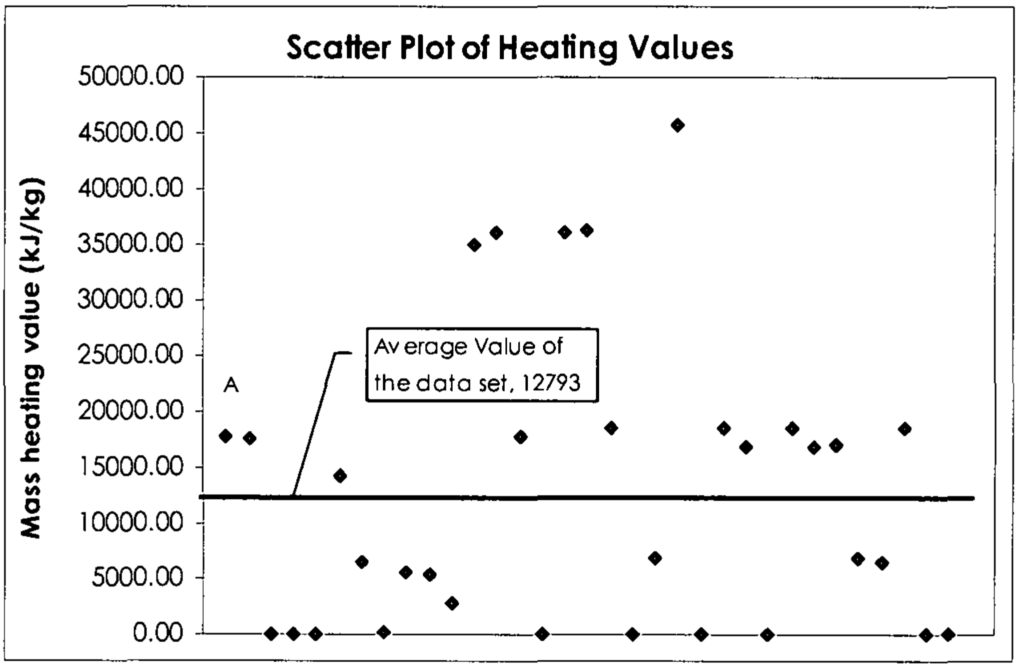


Figure 4.3 : Scatter plot of heating values for a 33 stream simulation

To determine the relative ranking of the heating value of stream A (17764.61kJ/kg) against the average for the data set (12793kJ/kg), a simple ratio is used. This can be expressed as:

$$I_e = \frac{\text{heating value of individual stream}}{\text{average heating value of all streams}} \qquad \text{Equation 4-4}$$

The I_e for stream A is 1.39. This also indicates that stream A has 39% more energy compared to the average of the system. When I_e for all 33 streams are calculated and relatively ranked, it can be observed in Table 4.4 that stream U is relatively highest in the rank of heating value.

Table 4.4 : I_e for 33 process streams within a simulation

Stream	I_e	Stream	I_e	Stream	I_e
U	3.58	B	1.38	K	0.22
Q	2.83	AB	1.33	H	0.01
P	2.83	X	1.32	AF	0.00
M	2.82	AA	1.32	AG	0.00
L	2.74	F	1.12	V	0.00
R	1.45	T	0.53	Y	0.00
W	1.45	AC	0.53	C	0.00
Z	1.45	G	0.50	D	0.00
AE	1.45	AD	0.50	E	0.00
A	1.39	I	0.43	O	0.00
N	1.39	J	0.42	S	0.00

Similar philosophy is extended to the other three properties in Equation 4-2 following Equation 4-5, Equation 4-6 and Equation 4-7.

$$I_P = \frac{\text{pressure value of individual stream}}{\text{average presssures of all streams}} \qquad \text{Equation 4-5}$$

$$I_\rho = \frac{\text{density value of individual stream}}{\text{average density of all streams}} \qquad \text{Equation 4-6}$$

$$I_{FL} = \frac{\Delta\text{FL of individual stream}}{\text{average } \Delta\text{FL of all streams}} \qquad \text{Equation 4-7}$$

The resulting dimensionless numbers can be used to clearly differentiate the streams when considering the properties individually. They can also be combined to give an index which reflects the severity of a process stream in the case of a leakage leading to a fire and/or explosion. The combinatory index is expressed in Equation 4-8.

$$\text{PSI} = 10 \times (I_P \times I_\rho \times I_e \times I_{FL}) \qquad \text{Equation 4-8}$$

Since the resulting individual dimensionless numbers are in small numbers, a multiplier of 10 is used to enlarge the resulting multiplication product. This empirical multiplier has been determined to be suitable for the set of process chemicals used in this prototype. There may be a need to use other multipliers if other chemicals are considered.

Using Equation 4-8, the PSI for all the 33 stream in this particular case is calculated and tabulated in Table 4.5 below.

Table 4.5 : Relative Ranking of PSI for 33 process streams

Stream	I_e	I_r	I_P	I_{DFL}	PSI
F	1.12	2.79	2.23	0.38	26.50
K	0.22	2.67	0.61	4.25	15.44
N	1.39	2.73	0.07	0.19	0.48
G	0.50	0.01	2.23	2.13	0.30
A	1.39	2.78	0.04	0.19	0.26
B	1.38	2.82	0.02	0.19	0.15
U	3.58	0.01	1.01	0.28	0.09
AC	0.53	0.00	1.01	3.28	0.07
R	1.45	0.01	1.01	0.89	0.07
W	1.45	0.00	1.01	0.89	0.05
Z	1.45	0.00	1.01	0.89	0.05
AE	1.45	0.00	1.01	0.89	0.05
AD	0.50	0.00	1.01	2.13	0.05
T	0.53	0.00	1.01	3.28	0.04
J	0.42	0.00	0.56	3.42	0.03
X	1.32	0.00	1.01	1.22	0.03
AA	1.32	0.00	1.01	1.22	0.03
H	0.01	0.01	2.23	3.28	0.01
C	0.00	0.00	0.51	0.00	0.00
D	0.00	0.01	2.53	0.00	0.00
E	0.00	0.01	2.53	0.00	0.00
I	0.43	2.82	0.61	0.00	0.00
L	2.74	2.03	0.51	0.00	0.00
M	2.82	0.00	0.06	0.00	0.00
O	0.00	2.82	0.56	0.00	0.00
P	2.83	0.00	0.00	0.00	0.00
Q	2.83	1.98	0.53	0.00	0.00
S	0.00	0.01	2.53	0.00	0.00
V	0.00	0.00	0.00	0.00	0.00
Y	0.00	0.00	0.00	0.00	0.00
AB	1.33	0.00	0.00	0.00	0.00
AF	0.00	2.81	0.51	0.00	0.00
AG	0.00	2.64	0.06	0.00	0.00

Using this index, users can easily identify via relative ranking, that stream F and K will result in greater potential consequences should a leak develops. This is determined as a result of interaction of process parameters by virtue of the philosophy behind Equation 4-8. If previous Inherent Safety indices are used, it is not possible to pinpoint which stream would be most inherently unsafe. The PSI also helps to eliminate the last 15 streams from being considered in improvement efforts since any leak from these 15 streams will not result in a flammable mixture or subsequently cause explosion.

Even though this is a new concept being introduced in this research, its validity can be established by comparing with other proven methods. This is deliberated in Section 5.3.

4.2 Inherent Risk Assessment (IRA)

Inherent Risk Assessment (IRA) is a module within the Inherent Safety Intervention Algorithm presented in Figure 4.2. By virtue of definitions deliberated in Section 2.2 and summarized by Equation 2-2, the IRA has two major components to determine probability of an event and subsequently the consequences arising from it. The probability and the consequences of a particular process under examination is the direct result of the inherent properties of the chemicals involved, process condition etc. At such IRA in principle gives an estimation of risk inherent to the process being designed. The IRA result from the initial assessment can be used as a benchmark to determine the level of improvement after the design has undergone improvement steps as shown in Figure 4.2.

Even though IRA adopts the structured approach from QRA, the two methodologies have fundamental differences. The key different is the stage when the methods are applied. Traditional QRA is applied after detail engineering design has been completed when Process & Instrumentation Diagram (P&ID) is fully available. QRA also takes into consideration the historical site specified weather conditions and plant layout. In contrast to this, the IRA Module developed in this research can be used as early as process simulation begins during preliminary design stages in parallel with selection of process route and development of heat and material balances. Unlike QRA, the IRA does not account for safety control measures such as procedures and instrumented protective functions. It merely reflects the inherent risk due to the inherent properties of the chemicals involved and process conditions of the design.

Owing to the different timing that the two assessments are carried out, the results are used for different purposes. More often than not, QRA results are used for reasons presented in Section 2.2.1 while results for IRA can be used to provoke inherent safety modifications during process simulation stages. Process designer engineers have considerable flexibility to improve the design in simulation stage as the manhours and cost to do so is relatively little. IRA results are suitable to be used as a quantitative method to screen processes and improvements.

Since QRA exercise is very extensive in nature and requires significant amount of time (Table 2.6) to produce; only few selected credible cases are studied and documented. Due to the lack of integration between QRA software and process simulator, all process conditions information need to be manually transferred. The IRA is fully integrated with HYSYS and data transfer is automated and hence reducing the chances for error. With process simulator, IRA can evaluate multiple conditions in a short time. For instance, inherent risk before and after pressure modification and be promptly assessed.

From the discussions above it can be concluded that IRA and QRA are meant for complementing purposes and are used in different timing along the process design stages. IRA as it is cannot be used to replace QRA. Table 4.6 summarizes the key distinctions between QRA and IRA.

Table 4.6 : Comparison of QRA and IRA

Criteria	QRA	IRA
Stage to be applied	After completion of detail engineering design	During preliminary design / simulation stage
Purpose	To demonstrate or prove "safety case" for required by regulatory agencies	To proactively identify risk inherent to the design and guide its reduction by adopting inherent safety principles
Regulatory requirements	Required by regulatory agencies, for example Department of Occupational Safety & Health in Malaysia and the Health and Safety Executive in the UK	Presently there is no regulatory requirement
Information required	Process & instrumentation diagrams (P&ID), detail historical weather data	Simulation data and assumptions on piping and equipment sizing
Scenario	Only few credible scenario to be studied in detail	Basic scenario i.e. pipe or equipment leak
Duration of analysis	Relatively long. Refer to Table 2.6	Relatively quick as it is carried out in parallel with simulation work
Result representation	3-region Frequency-Number (FN) curve	2-region Frequency-Number (FN) curve

The inherent risk level calculated by IRA needs to be presented in a comprehensive and easily understood manner to promote its adoption by the industries. Since the FN curve presented in Section 2.3 has been in use as part of QRA for few decades and has been generally accepted as graphical representation of risk result, the same concept will be used in IRA to represent inherent risk. However slight modification is carried out by the present research. The FN curve for IRA uses only two regions instead of three regions. It can be noted that the region below the diagonal line in Figure 4.4 covers the two regions on "Tolerable if ALARP" and "Tolerable" of Figure 2.7. These two regions are not separately represented in an IRA result because during this stage, safety measures and control mechanism are not yet in place to reduce risk to ALARP.

Figure 4.4 is developed based on the numerical limits dividing intolerable and tolerable regions set by the Malaysia authorities (last row of Table 2.8). Should the inherent risk of a process route fall above the red diagonal line, then it is clear that the route is not acceptable unless subsequent modifications can bring it below the line. For designs that have risk level below the line initially, there is still room for further improvement, again by adopting the principles of inherent safety.

Apart from presenting in form of FN curve, inherent risk assessment results for explosions can also be presented as overpressure versus distance and damage as function of distance. This is further deliberated in Section 4.2.2.

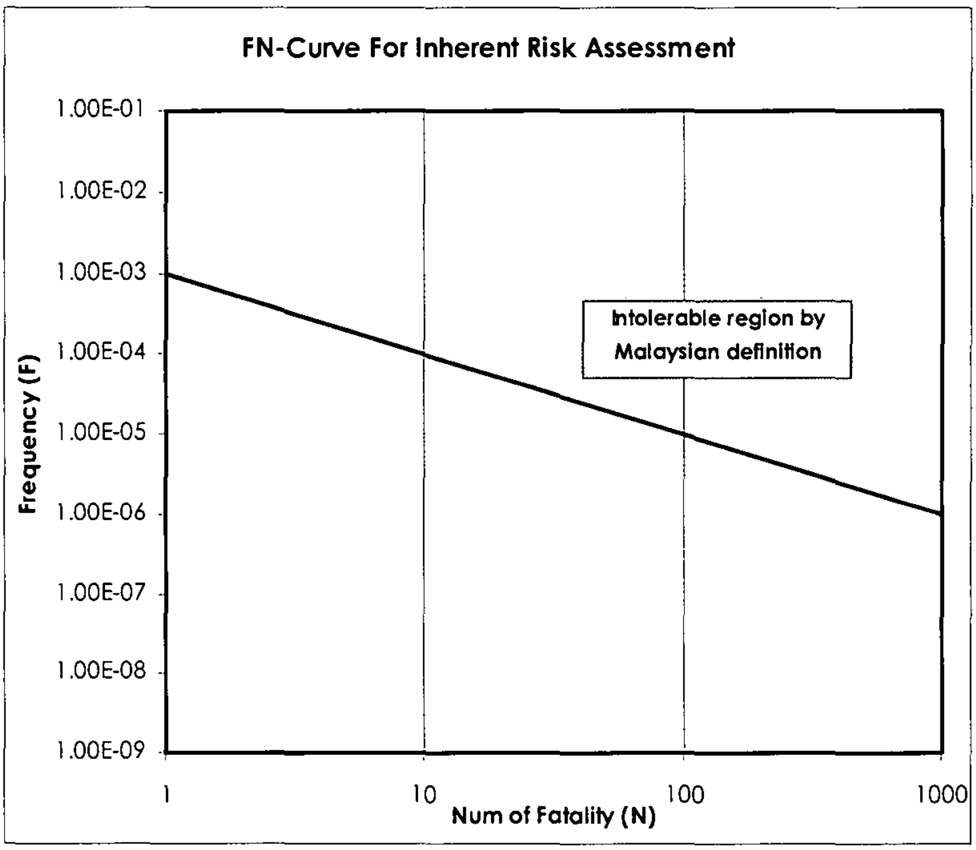


Figure 4.4 : FN curve to represent inherent risk

The following sections describe the two key component making up the IRA i.e. the probability and consequence modeling modules. These two modules have been based on modeling of explosion event. Future work subsequent to this research can develop similar module for other hazards such as fire, toxic release etc.

4.2.1 Integrated Explosion Event Tree (i-EET)

For the purposes of this research scope which address specifically explosion, an event tree is integrated within the Inherent Safety Intervention Framework to estimate probability of explosion following failure of predetermined components. This is known as the Integrated Explosion Event Tree (i-EET). i-EET is built based on existing published data from the industries as described in Section 2.4. Using the provided data, the present research derived an equation which related probability of ignition and explosion to the quantity of hydrocarbon leaked. Equation 3-23 is programmed into spreadsheet for integration with other modules.

i-EET adopts the principle of Event Tree Analysis (ETA) described in Section 2.1.4 to derive the frequency of an event. ETA is chosen over FTA due to its advantages in modeling events like explosion, which are sequential in nature. FTA implies sequence of event as irrelevant and has less obvious logic (Smith, 2003) compared to ETA. Furthermore, ETA has been used by many authoritative publications in this area of research including Lees (1996), Hendershot (1999) and CCPS (2000) to describe fire and explosion events.

i-EET in the IRA, like other modules, are only designed for explosions. While acknowledging that actual explosion event can be caused by slightly differing sequence of event, this research also tries to ensure consistency in all scenarios to enable useful comparison by fixing the ETA blocks in i-EET to follow a certain set of event. The sequence used in the i-EET is adopted from Hendershot (1999), who used it as a simplified basis to describe explosion. The ETA blocks in Figure 4.5 are not suitable for modeling other forms of hazards.

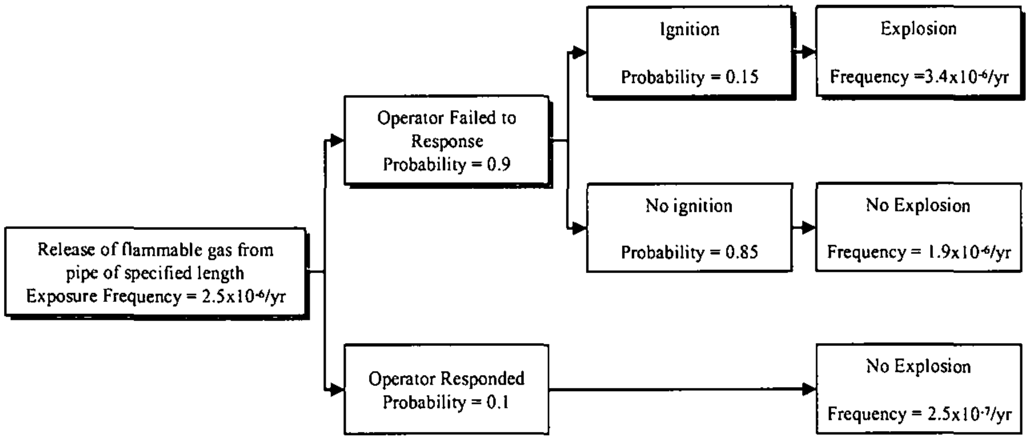


Figure 4.5 : Example of ETA blocks in i-EET

The frequency and probability data shown in this figure is only for illustrative purposes and are based on information in this example. An assumed case of a rupture in a 25meter long 300mm diameter pipe is used in this example. Base failure frequency is referred from database which is in Appendix B.

exposure frequency = base failure frequency x length x duration
= $1x10^{-7}$ (failure $year^{-1}$ m^{-1}) x 25(m) x 1 year
= $2.5x10^{-6}$ per year

Presently there is limited database on quantification of human reliability and Khan et. al. (2006) noted there is a need to advance this area of research and provide techniques that are useful in human error quantification to be embedded in QRA framework. In the i-EET, the present work based the operator failure to response within 5 minutes on studies by Cox (1990) which concluded a 0.9 chance. It is further assumed that the combustible mass determined by Equation 3-13 based on process information from HYSYS, is approximately 100 tons. From Equation 3-23, the probability of an explosion is 0.15. Multiplying the values in the shaded boxes, the frequency of an explosion resulting from an event in Figure 4.5 is $3.4x10^{-6}$ per year.

Users have the ability to change the numerical values in each of the ETA block in Figure 4.5. In this research, in order to ensure consistency in terms of steps leading to an explosion, the ETA sequence cannot be expanded or collapsed. Consistency is important so that various process options and modifications can be compared on equal basis from the event sequence aspect leaving only the chemical and process condition aspects as variables in the IRA.

4.2.2 Integrated Consequences Estimation Tool (i-CET)

Using the appropriate equations described in Chapter 3.0 and following the algorithm below, the consequences of an explosion can be estimated. Along with results from i-EET, risk information for the case can be generated and produced in the form of an FN curve. The FN curve from here is the ultimate output of step 3 in Figure 4.2 and is used in determining subsequent course of action.

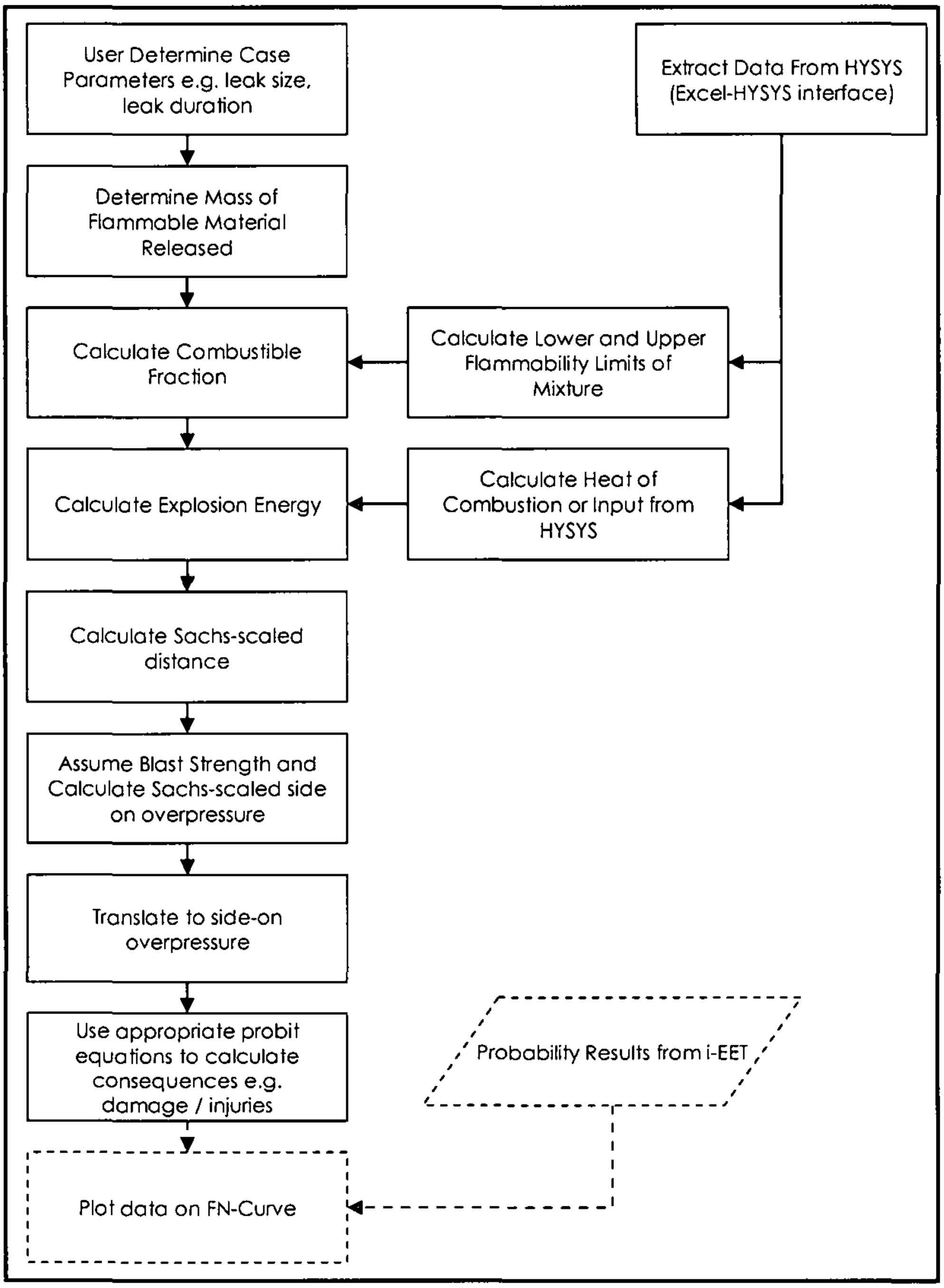


Figure 4.6 : i-CET based on TNO Multi Energy Correlation Method

Similar algorithm, up to using probit equation, had been deliberated by Chan (2004) using TNT Equivalent calculation methodology instead of TNO Multi Energy Correlation. The present author and Mohd. Shariff et. al. (2006) presented several case studies which demonstrated that consequences due to explosions can be assessed during the initial design stage. The results can be used by engineers to determine site locations of control buildings and also modify process conditions to ensure an inherently safer plant is being produced.

The present research adopts similar algorithm and enhanced it by using the TNO Multi Energy Correlation calculations, as described in Section 3.7, to calculate the blast wave strength. As observed in Figure 4.6, HYSYS process simulator provides the necessary data for initial calculations which will lead to determination of overpressure and subsequently consequences by use of probit equations. This link with HYSYS is developed using VBA coding and provides users efficient reassessment of consequences should the process parameters change.

Table 4.7 : Relevant equations for i-CET algorithm

Steps in Algorithm	**Equation**	**Remarks**
Calculate mass released	Equation 3-2 or Equation 3-3	Data from HYSYS
Calculate LFL & UFL of mixture	Equation 3-4 to Equation 3-7	Data from HYSYS
Calculate heat of combustion of mixture	Equation 3-8	Data from HYSYS
Calculate flammable fraction	Equation 3-13	
Calculate explosion energy	Equation 3-15	
Calculate Sachs-Scaled Distance	Equation 3-14	
Calculate Sachs-Scaled side on overpressure	Equation 3-18	Using relevant coefficients from Table 3.2 depending on blast curve selected. Typically curve 7 is used.
Consequences	Equation 3-22	Using relevant constants from Table 3.4

Number of death resulting from consequences of the explosion, calculated by i-CET, is multiplied with the probability of the event (calculated by i-EET) and presented in FN curve similar to the one shown in Figure 2.7. For non-death type of consequences the results are presented as a function of distance from the source of explosion. These representations are visualized in Figure 4.7 and Figure 4.8. The data for these figures are produced from a simulated explosion scenario in the reactor off gas stream of an acetic acid production process.

Figure 4.7 below shows that as the distance increases, the probability of damage to small equipment drops. For the case under illustration, the probability of damage to small equipment located at 500m away from the explosion is negligible while at distances less than 100m away, it is almost certain that small equipment will be damaged as a result of an explosion.

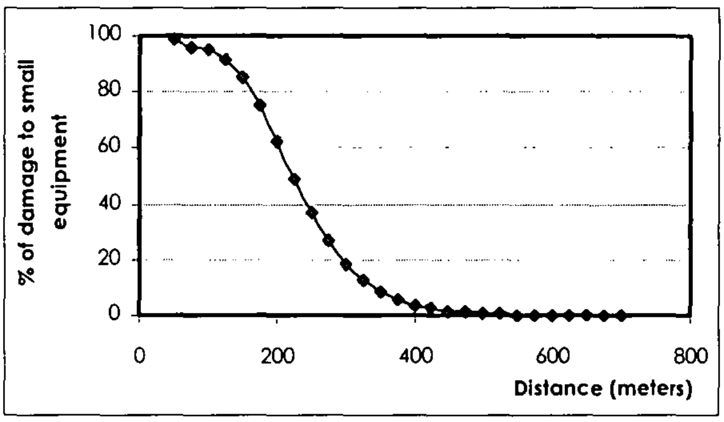


Figure 4.7 : Example of consequences (damage to small equipment) vs. distance

Figure 4.8 provides an illustration of probability of structural damage as a function of distance. For the case under discussion, it is observed that structural damage is a certainty at distances up to 200m from the source of explosion and rapidly decreases to a negligible value at approximately 700m from the explosion.

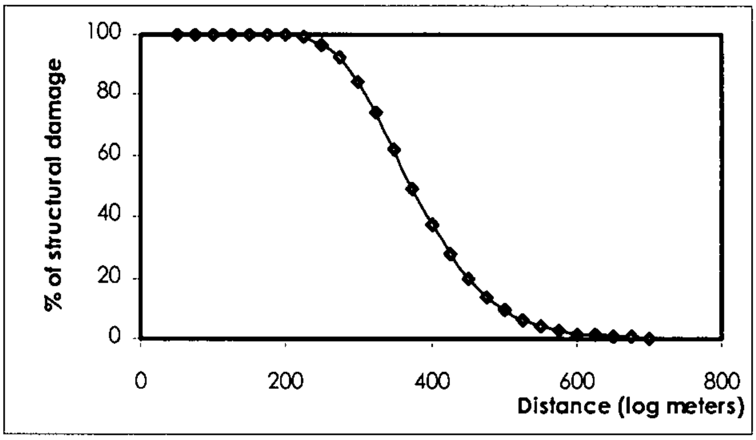


Figure 4.8 : Example of consequences (structural damage) vs. distance

Graphical representation of illustrated above, provides an early indication to engineers about the consequences of their design should there be an explosion. Using such information design engineers can intervene and improve the design as necessary. Chan (2004) in an earlier work presented the application of such information during the earlier process design stage in relocating control buildings to safer location.

CHAPTER 5

Validation and Case Studies

5.0 VALIDATION AND CASE STUDIES

This chapter presents validation of the indices proposed in Section 4.1 and case studies demonstrating the application of the Inherent Safety Intervention Framework in designing inherently safer processes.

Validation of the new indices proposed in Section 4.1 is carried out against published articles written by previous researchers and other calculated values. The most extensive process being referred by previous researchers is the methyl methacrylate acid (MMA). A newer study using acetic acid was also conducted. From the validation, it can be concluded that the new Process Route Index (PRI) produces very similar results to expert opinion and to large extent agree with previous inherent safety indices. However, minor discrepancies are noted and can be attributed to the fact that the new combinatory index accounts for parameter interactions that other indices do not.

Since this is the first work to develop an index to differentiate ISL between streams within a process, the validation of Process Stream Index (PSI) is carried against calculated parameter i.e. strength of explosion. It is demonstrated that the PSI is able to rank ISL of process streams and subsequently assist in prioritization of inherent safety modification efforts.

The case studies deliberated in this chapter demonstrate applications Inherent Safety principles described in section 2.6 into initial process design stages by utilizing the ISIF and tools developed in Chapter 4.0.

Through the case studies presented in this chapter, it is concluded that ISIF can potentially assist design engineers to quantify the potential risks up front during the initial design stages. It can also provide preliminary explosion consequence analyses. With such knowledge available to design engineers, inherently safer options can be selected and potentially result in a safer design.

However, the ISIF framework does not account for other factors which are often taken into parallel consideration for process modification and design changes such as lifecycle cost analyses. The ISIF framework proposed in this research also lacks the capability to automatically propose alternatives for modification. Human intervention (design engineers) is still required to generate process modification alternatives. ISIF can be used to assess individual merits from safety perspective for each alternative.

5.1 Validation of Process Route Index with MMA Process

In the first attempt to develop inherent safety index, Lawrence (1996) used various routes of methyl methacrylate acid (MMA) as case study. Details of the Prototype Index for Inherent Safety (PIIS) have been described in Section 2.7.1 of this thesis. M. Rahman et. al. (2005) published a paper in which the ISI by Heikkilä (1999) and i-Safe by Palaniappan (2003) were used to rank the MMA. The results were compared against results from PIIS and expert panel.

When analyzing result determine by Heikkilä's ISI, it is noted that ISI was not able to distinguish the inherent safety level of the TBA and i-C4 routes. However it is in agreement with expert opinion that C2/PA is inherently most unsafe. Results produced using i-Safe, is in agreement with the rest in terms of identifying TBA as the safest route and C2/PA is the most unsafe. The inaccuracy of indices is related to the differences of their sub index structure and properties. In PIIS, the evaluation is based on the reaction steps and it does not consider separation sections directly at all. The reaction hazards are not taken into account directly but through pressure, temperature, physical properties and yields. All index methods up to this point, suffer to some extent from simplifications and lack of sub index interaction. Indices prior to the present research are based on physical and/or chemical properties of individual chemicals in the process. The new Process Route Index (Section 4.1) proposed in this research, on the other hand, reflects actual stream properties by accounting for effects of temperature, pressure, flammability and fluid density. Derivation of the new combinatory index had been presented in Chapter 4.1.

Results from using the three indices and expert opinion have been tabulated and used as a comparison (Table 5.1) to the new PRI proposed in the present research (right most column).

The MMA processes were simulated in HYSYS and analyzed using this index. Figure 5.1 is the print screen of the MS Excel spreadsheet which shows the PRI for the last of the MMA process routes. The corresponding HYSYS simulation screen is provided in Figure 5.2.

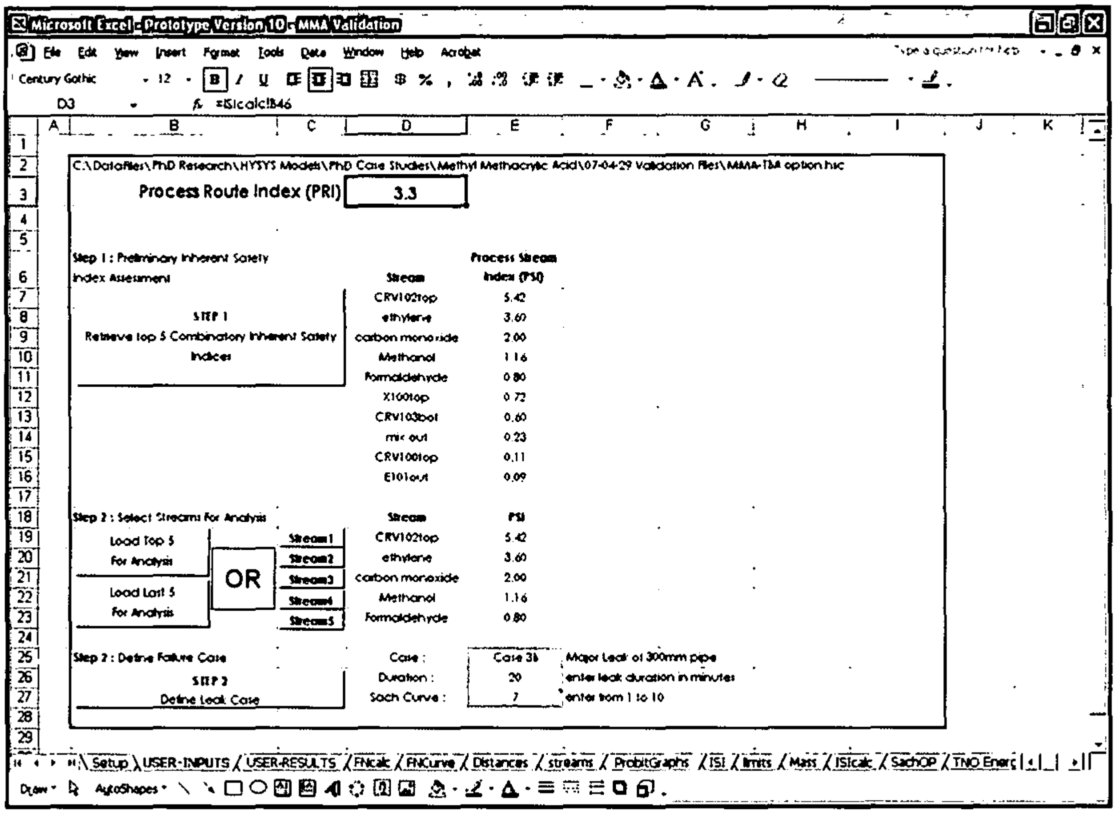


Figure 5.1 : Print screen showing PRI result for one of the MMA route

The respective PRI results for the four routes were provided in the right most column of Table 5.1 and the relative rankings (Section 2.1.6) based on this index are within brackets ( ). Using similar approach as previous techniques, the process with lower rank number is deemed to be inherently safer.

Table 5.1 : Ranking of MMA processes by various indices and expert opinion

Methyl Methacrylate (MMA) Process Routes	Lawrence – PIIS	Experts Opinion	Heikkilä – ISI	Palaniappan – i-Safe	**Process Route Index (rank)**
Ethylene via methyl propionate based route (C2/MP)	3	3	2	2	**76.5 (4)**
Ethylene via propionaldehyde based route (C2/PA)	4	4	3	5	**32.3 (3)**
Isobutylene based route (i-C4)	2	2	1	3	**9.1 (2)**
Tertiary Butyl Alcohol based route (TBA)	1	1	1	1	**3.3 (1)**

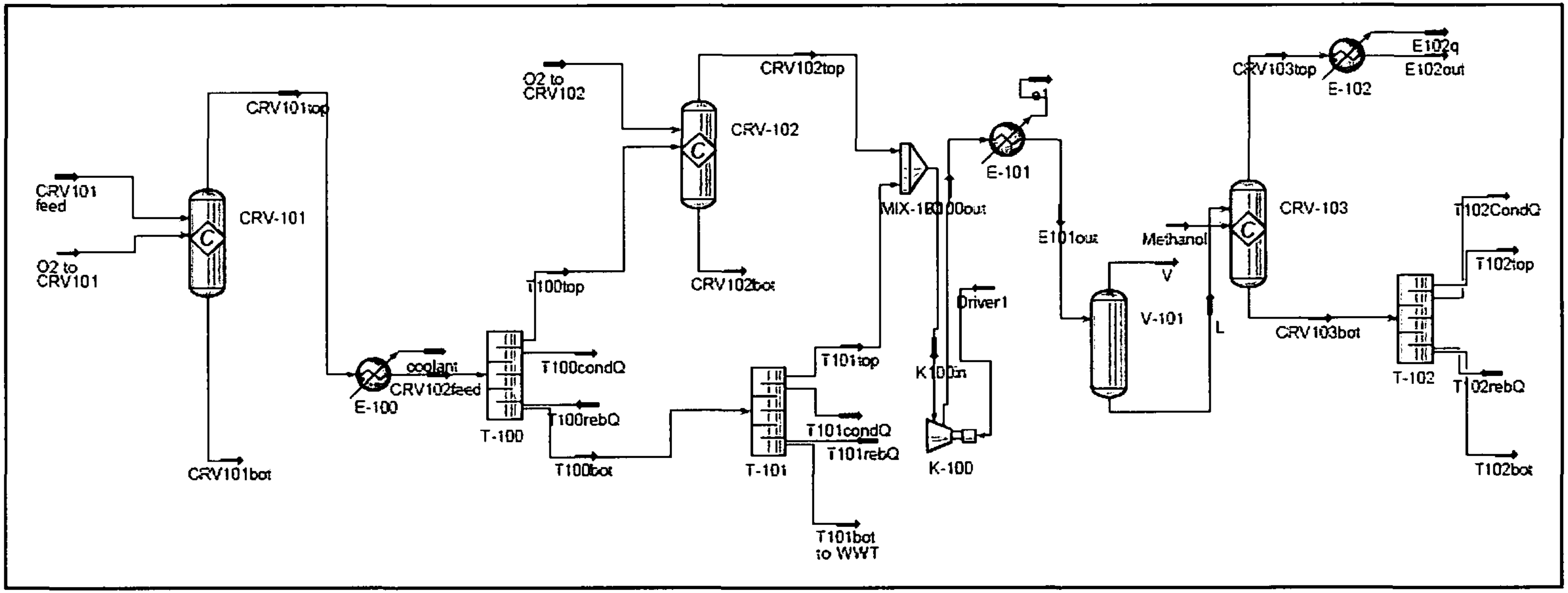


Figure 5.2 : HYSYS simulation of TBA route for MMA production

This comparison shows the new PRI proposed by the present research produces results that mirror expert opinion as well as the PIIS by Lawrence (1996). This is numerically represented by correlation coefficient tabulated below. The correlation coefficients are calculated using relative rankings produced by indices in Table 5.1. Correlation coefficient of 1.0 (unity) concludes that the two data sets are linearly related i.e. having same trends. In this case it can be statistically concluded that relative ranking based on PRI result is a close match to PIIS and expert opinion. PRI is closely related to ISI and to a lesser degree, linked to i-Safe.

Table 5.2 : Correlation coefficients of MMA process routes relative rankings

	Lawrence – PIIS	Experts Opinion	Heikkilä – ISI	Palaniappan – i-Safe
Correlation Coefficient For PRI Against Other Indices and Expert Opinion	0.8	0.8	0.7	0.4

One of the contributing factors to the difference with ISI is the fact that The PRI is able to distinguish between TBA and i-C4 routes, which ISI failed to.

5.2 Validation of Process Route Index with Acetic Acid Process

Palaniappan et. al. (2004), published a paper demonstrating the use of i-Safe in selecting the inherently safer process routes for acetic acid. The Overall Safety Index proposed by Palaniappan (2003) is the sum of Overall Reaction Index and the Overall Chemical Index. Details of this technique are deliberated in Section 2.7.3. The results from this paper are presented in the middle column of Table 5.3. It is noted that i-Safe failed to distinguish between Butane Oxidation and the HP Methanol Carbonylation routes. Both the routes scored 20 for Overall Safety Index in i-Safe.

The present research also conducted a benchmark with results from Palaniappan as tabulated below. Both techniques indicate that ethanol oxidation route as the safest to produce acetic acid, followed by ethylene oxidation. The present technique ranks the acetaldehyde oxidation as third and low pressure (LP) methanol as fourth. Additionally, the present technique is able to differentiate between butane oxidation route and high pressure (HP) methanol carbonylation route. Calculated values using i-Safe by Palaniappan and PRI proposed in this research and relative ranking based on these values are provided in Table 5.3.

Table 5.3 : Inherent Safety Indices for Acetic Acid routes and relative rankings

	Overall Safety Index (Palaniappan)			Process Route Index (present research)	
Acetic Acid Production Routes	**Calculated value**	**Relative Ranking**		**Calculated value**	**Relative Ranking**
Acetaldehyde Oxidation	18	4		0.4468	3
Butane Oxidation	20	5		2.2904	5
Ethanol Oxidation	14	1		0.2060	1
Ethylene Oxidation	15	2		0.4453	2
HP Methanol Carbonylation	20	5		41.8745	6
LP Methanol Carbonylation	17	3		0.7355	4

With a correlation coefficient of 0.92 between the relative rankings, it can be concluded that the PRI proposed in the present research is comparable to previously published work.

5.3 PSI Validation with Explosion Energy

This case study is aimed at testing the proposed Process Stream Index (PSI) using the same streams that were analyzed using Heikkilä's Inherent Safety Index. The three streams are analyzed using methods described in Equation 4-4 to Equation 4-8.

Table 5.4 : Calculation of Process Stream Index

Stream	Contributing Indices to the Process Stream Index							
	Pressure (average= 1.81)		Density (average= 502)		Heat of combustion (average= 12062)		Δ(UFL-LFL) (average= 13.84)	
	bar	I_P	kg/m3	I_ρ	kJ/kg	I_e	%	I_{FL}
A	2	1.10	1.97	0.001	18568	1.54	23.59	1.70
B	5	2.76	3.42	0.001	0	0	0	0
C	2	1.10	3.24	0.001	45831	3.80	7.50	0.54

$$PSI_{streamA} = 10 \times (I_P \times I_\rho \times I_e \times I_{FL}) = 10 \times 1.1 \times 0.001 \times 1.54 \times 1.7 = 0.1138 \quad \text{Equation 5-1}$$

$$PSI_{streamB} = 10 \times (I_P \times I_\rho \times I_e \times I_{FL}) = 10 \times 2.76 \times 0.001 \times 0 \times 0 = 0 \quad \text{Equation 5-2}$$

$$PSI_{streamC} = 10 \times (I_P \times I_\rho \times I_e \times I_{FL}) \quad \text{Equation 5-3}$$
$$= 10 \times 1.1 \times 0.001 \times 3.8 \times 0.54$$
$$= 0.1467$$

From these calculations, it is observed that Stream C is relatively most dangerous should there be a leak and combustion. This is confirmed by explosion energy calculated using TNO methodology for a choked release of the stream materials shown in Table 5.5.

Table 5.5 : Process Stream Index Compared to Explosion Energy

Stream	Process Stream Index	Explosion Energy
A(feed to R100)	0.1138	3.66E+09
B (hp air)	0	0
C (Propylene)	0.1467	1.13E+10

From this work, it can be concluded newly proposed PSI in this research, is able to reflect the interaction of various parameters within individual process stream to account for its Inherent Safety Level. Using the same methodology presented above, other validations are carried out against few other processes with larger number of process streams involved in each simulation. Table 5.6 presents PSI for 21 process streams in a Natural Gas Liquid (NGL) plant simulation compared against the explosion energy calculated for the respective streams. Using the correlation coefficient calculations (function in MS Excel) it is determined that PSI and explosion energy for the 21 streams are in good agreement. The correlation coefficient for the two data sets is 0.92

Table 5.6 : PSI and explosion energy for NGL simulation process streams

Stream	PSI	Explosion Energy		Stream	PSI	Explosion Energy
Feed2	27.57	5.57E+12		To V-2504	4.73	2.94E+12
Reflux	25.97	6.10E+12		To E-2405	4.02	2.5E+12
recycle	25.94	6.10E+12		To P-2505	3.79	2.75E+12
To P-2401	25.43	6.04E+12		To E-2403	3.69	2.28E+12
Feed3	11.88	3.76E+12		Feed	3.62	2.12E+12
Gasoline	6.74	1.20E+12		To E-2451	0.83	1.03E+12
ex P-2505	5.13	3.41E+12		NGL	0.32	6.36E+11
Reflux to C-2502	5.13	3.41E+12		To V-2503	0.22	6.42E+11
EX P-2506	5.04	3.30E+12		To E-2508	0.14	5.3E+11
To P-2506	4.73	2.94E+12		To E-2510	0.12	4.7E+11
To V-2402	4.36	2.56E+12				

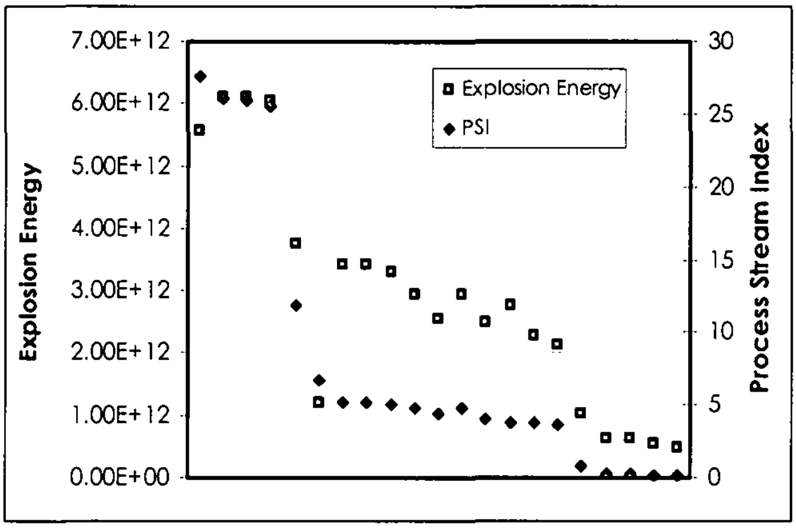


Figure 5.3 : PSI and explosion energy for NGL simulation

The following validation case is based on 10 process streams in propane refrigeration. The data sets of PSI and explosion energy are also well correlated. The correlation coefficient for the data set is 0.90.

Table 5.7 : PSI and explosion energy for Propane refrigerant process streams

Stream	PSI	Explosion Energy		Stream	PSI	Explosion Energy
Outlet	90.16	1.69E+12		Outlet 4th stage	26.38	1.15E+12
7	66.63	1.448E+12		8	23.53	1.08E+12
Inlet	36.09	1.074E+12		Side load 4th stage	3.23	4.12E+11
To E-91445	28.55	1.22E+12		Inlet 4th stage	3.08	4E+11
To V-91408	28.49	1.229E+12		Outlet 3rd stage	2.97	3.91E+11

Another hydrocarbon processing i.e. fractionation case is used in validation and the data sets are presented in Table 5.8. The PSI and explosion energy for the 11 streams in the fractionation simulation has correlation coefficient of 0.96. This again concludes that PSI provides good reflection of the explosion energy within respective streams.

Table 5.8 : PSI and explosion energy for hydrocarbon fractionation process streams

Stream	PSI	Explosion Energy		Stream	PSI	Explosion Energy
P-1506 Outlet	32.28	7.733E+12		C-1503 Ovhd	9.37	3.326E+12
C4 Rundown	32.28	7.733E+12		E-1405 Ovhd	7.74	3.634E+12
P-1401 Outlet	29.27	5.692E+12		Feed to E-1405	5.06	2.543E+12
Feed to V-1402	28.99	5.666E+12		NG to E-1403	4.83	2.456E+12
C-1502 Ovhd	13.51	3.59E+12		C-1504 Ovhd	4.03	2.729E+12
C3 Rundown	9.48	3.393E+12				

Using similar methodology and calculation as the above validation case studies, Table 5.9 presents 8 process streams from an acrolein simulation. Unlike the cases presented above, acrolein production is a petrochemical process. The two sets of data i.e. PSI and explosion energy has correlation coefficient of 0.86. This again shows that the new index proposed in this research is able to reflect actual explosion energy and at such is a good indicator for explosion risk.

Table 5.9 : PSI and explosion energy for Acrolein process streams

Stream	PSI	Explosion Energy		Stream	PSI	Explosion Energy
A	356.71	1.61E+12		E	152.09	2.30E+12
B	155.49	2.45E+12		F	104.26	1.95E+06
C	155.47	2.45E+12		G	68.53	8.51E+05
D	155.47	2.45E+12		H	0.08	2.78E+04

The four cases presented above demonstrate that PSI developed in this research based on the philosophy deliberated in Section 4.1, is in close correlation with explosion energy calculated for respective streams within a simulation. The summary is presented in Table 5.10. PSI can be used to rank process streams to identify those with higher scores to be given priority for inherent safety modifications. This point is further illustrated in the following chapter by means of case studies.

Table 5.10 : Summary of PSI and explosion energy correlation coefficients

Process	Number of Streams	Correlation coefficient between PSI and explosion energy in streams
NGL	21	0.92
Propane Refrigerant	10	0.90
Fractionation	11	0.96
Acrolein	8	0.86

5.4 Simplification of Acrylic Acid Production Process to Improve Inherent Safety Level

The validation cases above, have clearly demonstrated the application of ISIF in ranking various process routes and hence allowing selection of inherently safer processes to produce methyl methacrylate (MMA) and acetic acid. The key differences in the cases presented in Sections 5.1 and 5.2 are feedstock chemicals and subsequent reaction conditions. It can be surmised that substitution (one of the Inherent Safety principles) of feedstock can influence and improve the overall ISL.

This present set of case studies is based on acrylic acid process simulation. This case study is aimed to demonstrate the application of the 2t-ISI to quantify level of inherent safety in different variations of the same process before and after inherent safety modifications.

Acrylic acid is commonly produced by partial oxidation of propylene. In this route, the usual mechanism for producing acrylic acid utilizes a two step process in which propylene is first oxidized to acrolein and then further oxidized to acrylic acid. The reactions are summarized in Table 5.11. Equation 5-6 to Equation 5-8 are side reactions that take place alongside the two main reactions. The base case flow diagram for this process is provided in Figure 5.4.

Table 5.11 : Acrylic Acid Production Reactions

Reaction	**Stoichiometric Equation**	**Heat of Reaction (kJ/kg mole)**	
Oxidation of propylene to acrolein	$C_3H_6 + O_2 \rightarrow C_3H_4O + H_2O$	-332347	Equation 5-4
Oxidation of acrolein to acrylic acid	$C_3H_4O + 0.5O_2 \rightarrow C_3H_4O_2$	-265282	Equation 5-5
Side reaction	$C_3H_4O + 3.5O_2 \rightarrow 3CO_2 + 2H_2O$	-1592452	Equation 5-6
Side reaction	$C_3H_4O + 1.5O_2 \rightarrow C_2H_4O_2 + CO_2$	-757951	Equation 5-7
Side reaction	$C_3H_6 + 4.5O_2 \rightarrow 3CO_2 + 3H_2O$	-1924799	Equation 5-8

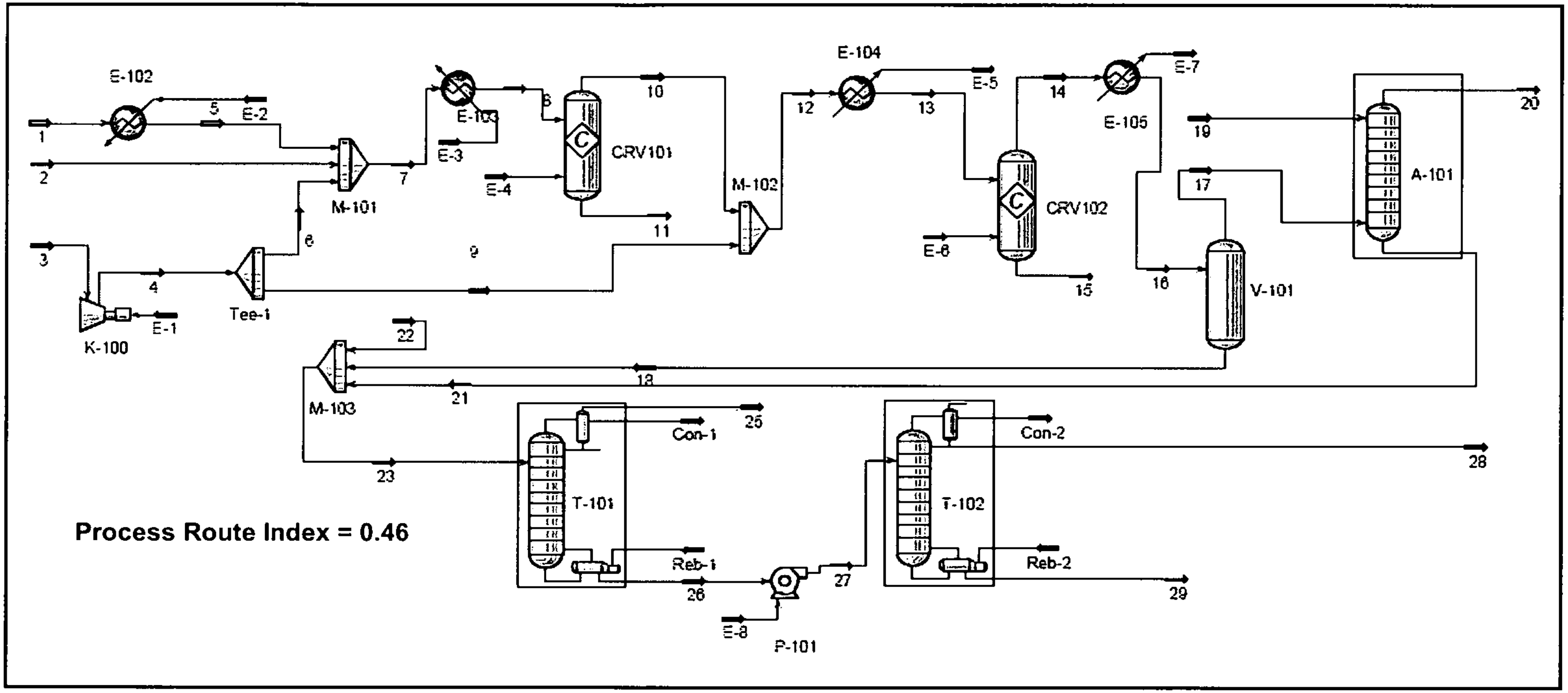


Figure 5.4 : Acrylic Acid production preliminary simulation

This initial process simulation uses two reactors shown as CRV101 and CRV102 in Figure 5.4. CRV 101 is where propylene is partially oxidized to acrolein in accordance with Equation 5-4. In CRV102, Equation 5-5 is the predominant reaction converting acrolein to acrylic acid. Reactions described by Equation 5-6 and Equation 5-7 also occur in CRV102.

Gaseous product from CRV102 is partially quenched and passed through scrubber tower A101. Liquid stream from bottom of A101 is combined with liquid stream from reactor CRV102 and passed to two distillation columns in series for purification. T101 separates water from the mixture of water and acrylic acid in stream 23 to a purity of 99.6%. In this preliminary design T102 is provided to further purify acrylic acid from 99.6% to 99.9% by simple distillation. Process Route Index (PRI) calculated for this preliminary simulation is 0.46.

PSI calculation shows that stream 18 has the highest score amongst the process streams in the simulation. This indicates that the stream will potentially cause the most damage should an explosion occur. Inherent Risk Assessment (IRA) is carried out to estimate the risk which is inherent to the process conditions and composition of this steam based on a set of assumptions. This set of assumption is made to derive probability factor in the risk component. The leak scenario is assumed to originate from 300mm diameter pipe and stopped within 20 minutes. The consequence (death) is calculated following the i-CET algorithm in Figure 4.6 while probability of explosion is calculated using equations presented in Section 3.9. It has been determined that the frequency (probability) of such an event is approximately once in ten thousand years and in such an incident, calculation shows that more than one but less than two death can result as a consequence. The frequency (F) and the number of fatality (N) are plotted on a simplified FN curve (Figure 5.5) which has two regions instead of three regions. The background of this has been deliberated in Section 4.2. From Figure 5.5, it can be concluded the Inherent Risk due to the process conditions and stream composition is not above the intolerable limits defined by Malaysian authorities.

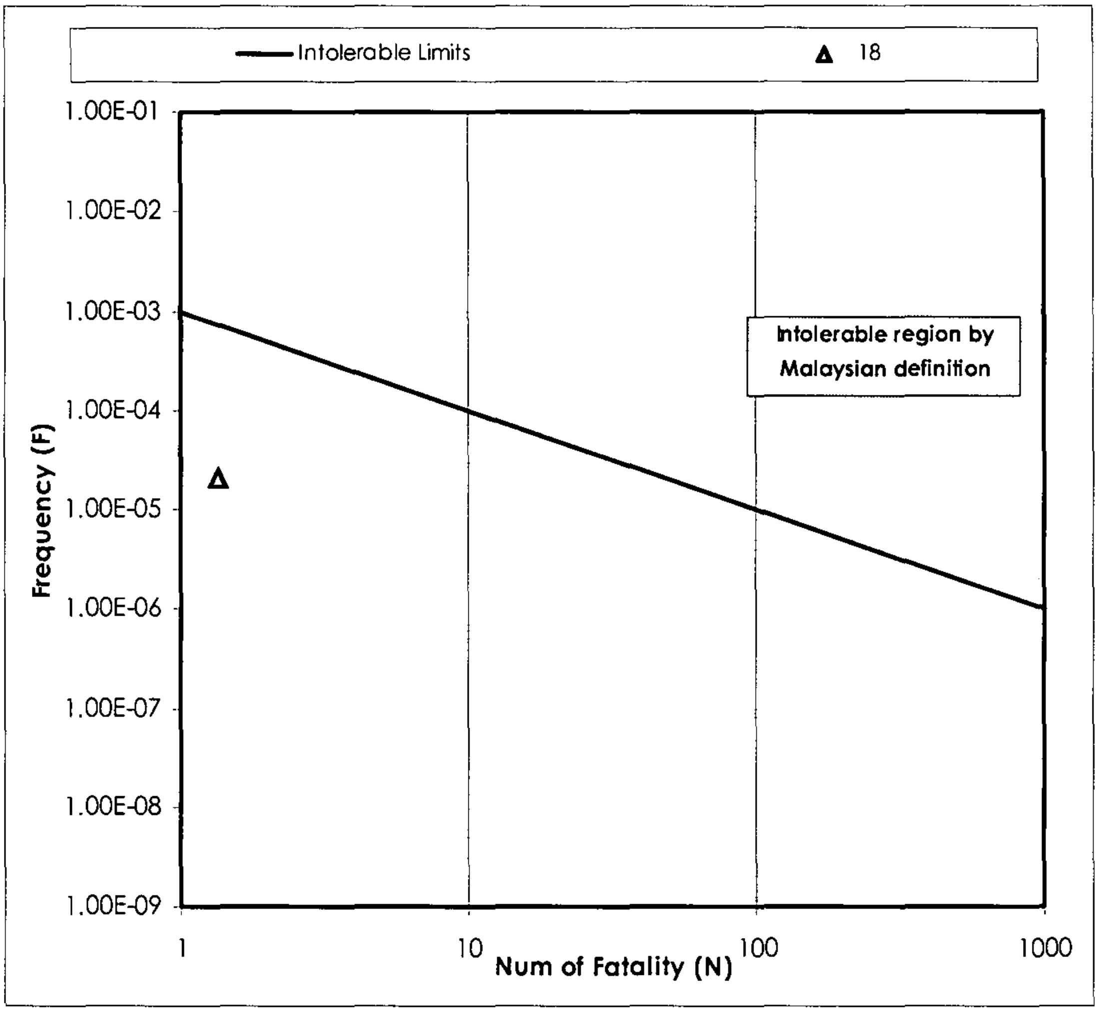


Figure 5.5 : FN curve for IRA of acrylic acid process

Following the algorithm in Figure 4.2, even though the IRA meets government requirement, proactive risk reduction by means of applying inherent safety modification can still be carried out. However, the modifications are subjected to the simulation maintaing its original design intent and producing products as per original specification. This research used the PSI to prioritize the streams in order to narrow down the modification efforts. PSI for all 28 streams are tabulated below and the top ten streams are circled in dots in Figure 5.6

Table 5.12 : PSI for 28 streams in Acrylic Acid base case

Stream	PSI		Stream	PSI		Stream	PSI		Stream	PSI
18	13.54		10	0.12		14	0.04		17	0.00
23	12.52		1	0.11		25	0.00		15	0.00
27	1.16		26	0.10		22	0.00		11	0.00
29	0.44		16	0.09		20	0.00		9	0.00
28	0.20		5	0.08		19	0.00		6	0.00
13	0.13		7	0.08		4	0.00		3	0.00
12	0.12		8	0.05		21	0.00		2	0.00

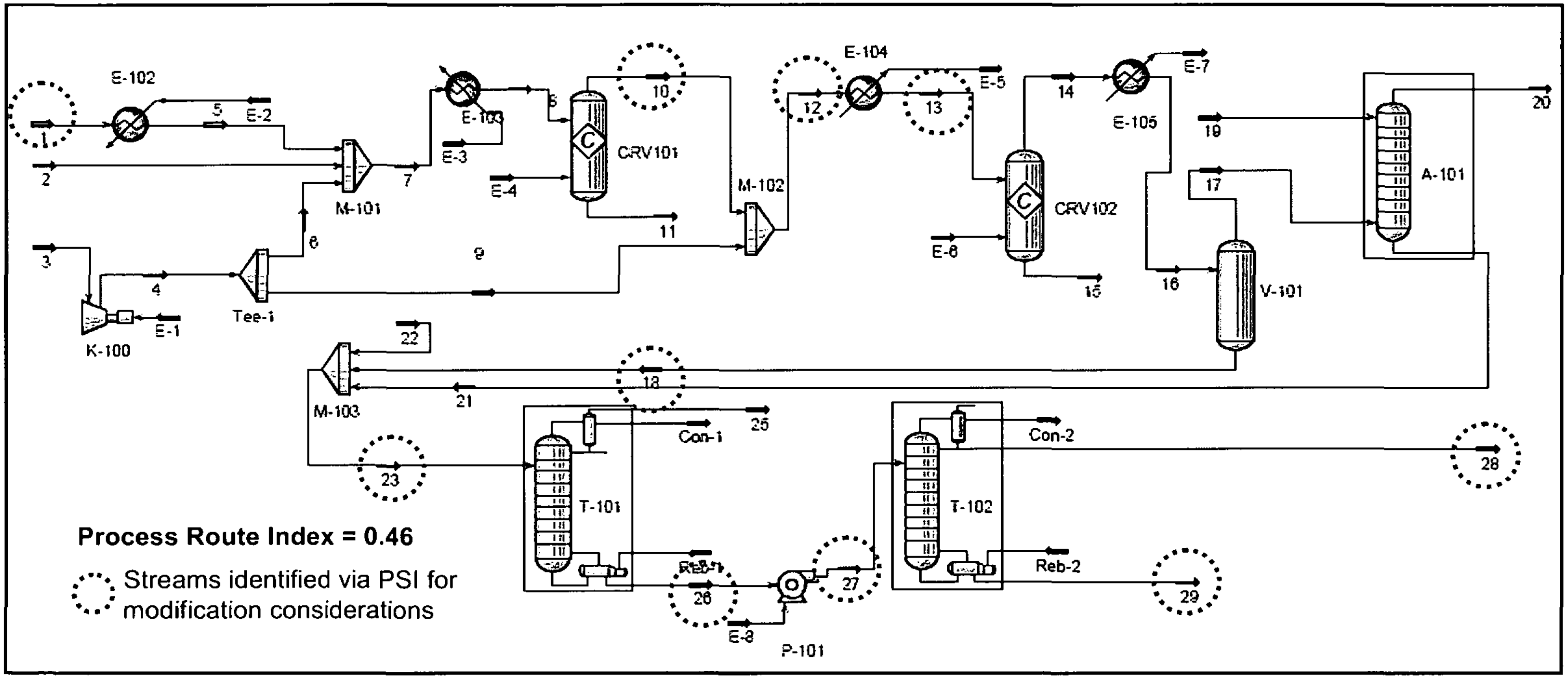


Figure 5.6 : Streams with high PSI

It is noted from Figure 5.6, that these streams are around the two reactors and two distillation columns. It is also observed that the circled streams are adjacent to each other. This means that modification to any one of the streams will also impact the adjacent steams and thus bring higher positive response to inherent safety modifications. At such modification efforts are guided towards these two areas instead of other parts of the simulation like scrub column or the feedstock sections. The present research attempts to improve the situation by adopting a strategy to eliminate the offending stream where possible. This can be achieved by adopting one of the principles of inherent safety, which is to simplify the process. Based on the guideline provided in Table 2.12, simplification means avoiding complexities such as multi-unit operations.

The first modification is to simplify the purification section by reducing the number of distillation column. In the base case, two distillation columns are used to purify the product. By increasing the number of trays in T-101 from original 40 to 50 and reducing the solvent from stream 22, the product purity in stream 26 increased to meet the production requirement of 99.9% purity. In this exercise, one pump and distillation column with its accessories are eliminated, hence simplifying the process. The simplification result in a revised simulation as illustrated in Figure 5.7. This revised design has PRI of 0.38. Improvement over the base case can be calculated using

$$\text{improvement} = \left(1 - \frac{\text{PRI of modified process}}{\text{PRI of original process}}\right) \times 100\% \qquad \text{Equation 5-9}$$

Using Equation 5-9, the modified design shown in Figure 5.7 has improved by approximately 17% compared to base case.

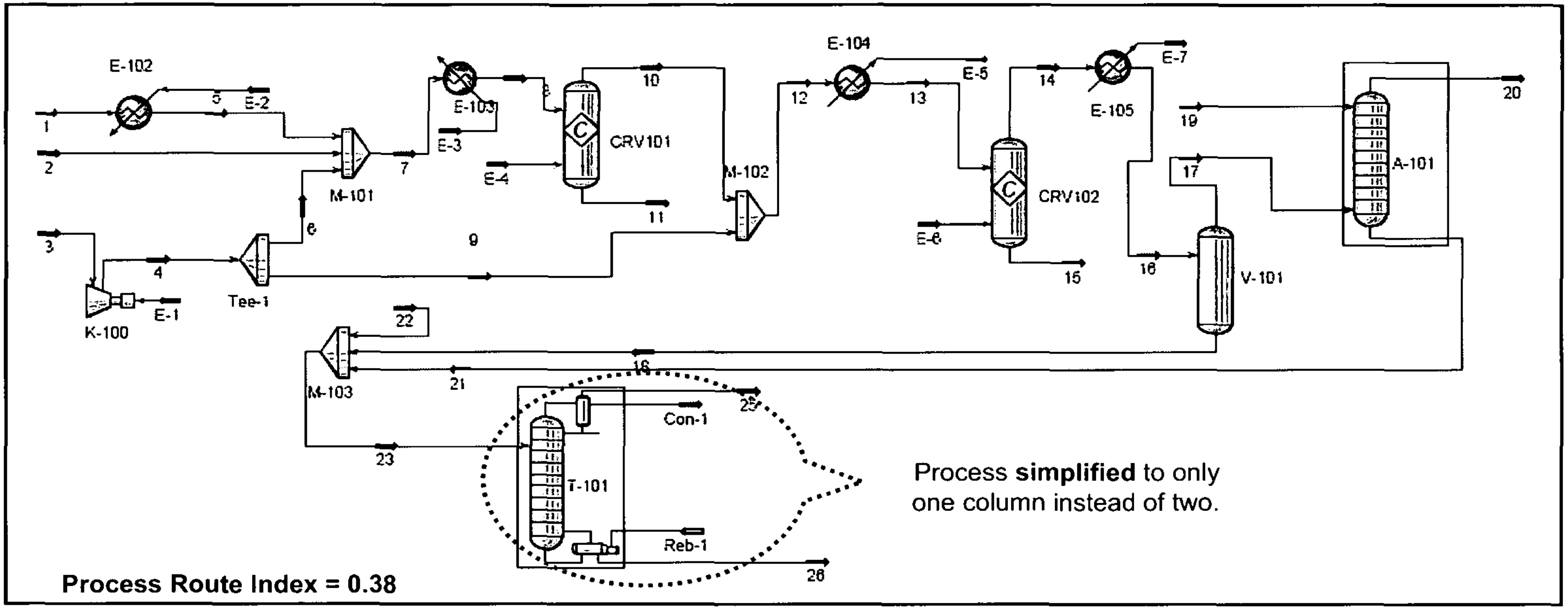


Figure 5.7 : Acrylic Acid Process with one column, two reactors

The second case study is carried out to study the impact of simplifying the reactor section instead of the purification section of the acrylic acid process presented above. The modified simulation is illustrated in Figure 5.8. Note a single reactor is used in place of two reactors. This modification also reduced the number of equipment count and this can translate in to possible lower capital cost and operating cost as well as improved reliability. Two major equipments eliminated are reactor and one heat exchanger. In this case the two distillation columns from base case are not modified.

PRI for this modified process is 0.29. This is a considerable improvement in terms of the overall process inherent safety level. Compared to the base case PRI of 0.46 this is an improvement of approximately 37% (1-(0.29/0.46)x100%).

In this particular process simulation, it can be observed that modification to the reactor section results in greater improvements compared to modification at the purification section. A third attempt to improve the inherent safety of this process is by combining the first and second modification into a revised design which uses only one reactor and one distillation column.

The revised PRI for the further simplified acrylic acid process is 0.25. When compared to the base case, the latest case illustrated in Figure 5.9, level of inherent safety has been improved by approximately 46%. All the PRI calculated are summarized in Table 5.13.

Table 5.13 : Summary of PRI for three options and relative improvements

Case	Reference	PRI	Improvement over base case
Base	Figure 5.4	0.46	Not applicable
Two Reactors One Column	Figure 5.7	0.38	17%
One Reactor Two Column	Figure 5.8	0.29	37%
One Reactor One Column	Figure 5.9	0.25	46%

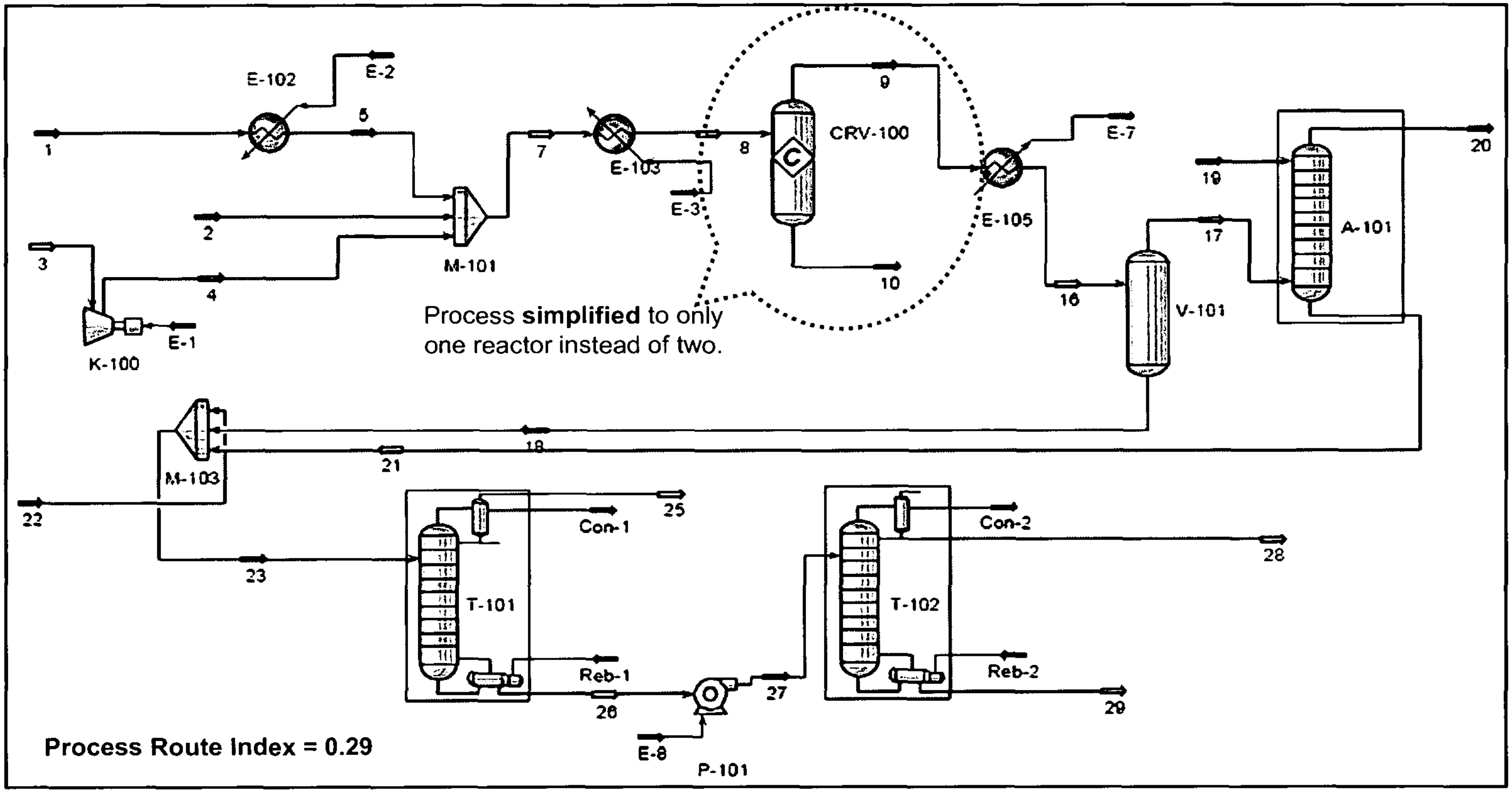


Figure 5.8 : Simplified Acrylic Acid using one Reactor, two columns

Apart from the improved level of inherent safety in the design, the modification also brought about small increment of production increase while using the same amount of feedstock. The increment is documented in Table 5.14. However this is a specific observation and should not be generalized to other processes.

Table 5.14 : Incremental acrylic acid produced resulting from modifications

Case	**Acrylic Acid (kg/hr) flow**	
	Inlet to V101	Final Product
Base	6321	6257
Two Reactors One Column	6321	6294
One Reactor Two Column	6380	6258
One Reactor One Column	6380	6345

The improvement in the level of inherent safety as presented above comes with certain tradeoffs. In an attempt to reduce the complexity of reactor by using only one reactor, all reactions described in Table 5.11 take place in CRV100, resulting in higher reactor exit temperature. The temperature in stream 9 in Figure 5.8 is 1044°C while the temperature in stream 10 of Figure 5.4 is only 320 °C. This translates into more expensive vessel and piping material as well as higher cooling duty required of the downstream heat exchanger. In the second modification, the cost of T101 will increase as the number of trays increase by 10. Even though safety is of paramount importance, the cost of modification above needs to be determined and the impact on project economics needs to be assessed.

From this set of case studies it can be concluded that every modification brought about positive feedback in terms of improved level of inherent safety as observed in the improved PRI for each revised process. However, presently the guideline as to how extensive should the modification be undertaken has yet to be developed. In the present research, the author uses checks for product quantity and quality to ensure the simulation cases do not deviate from original design intent.

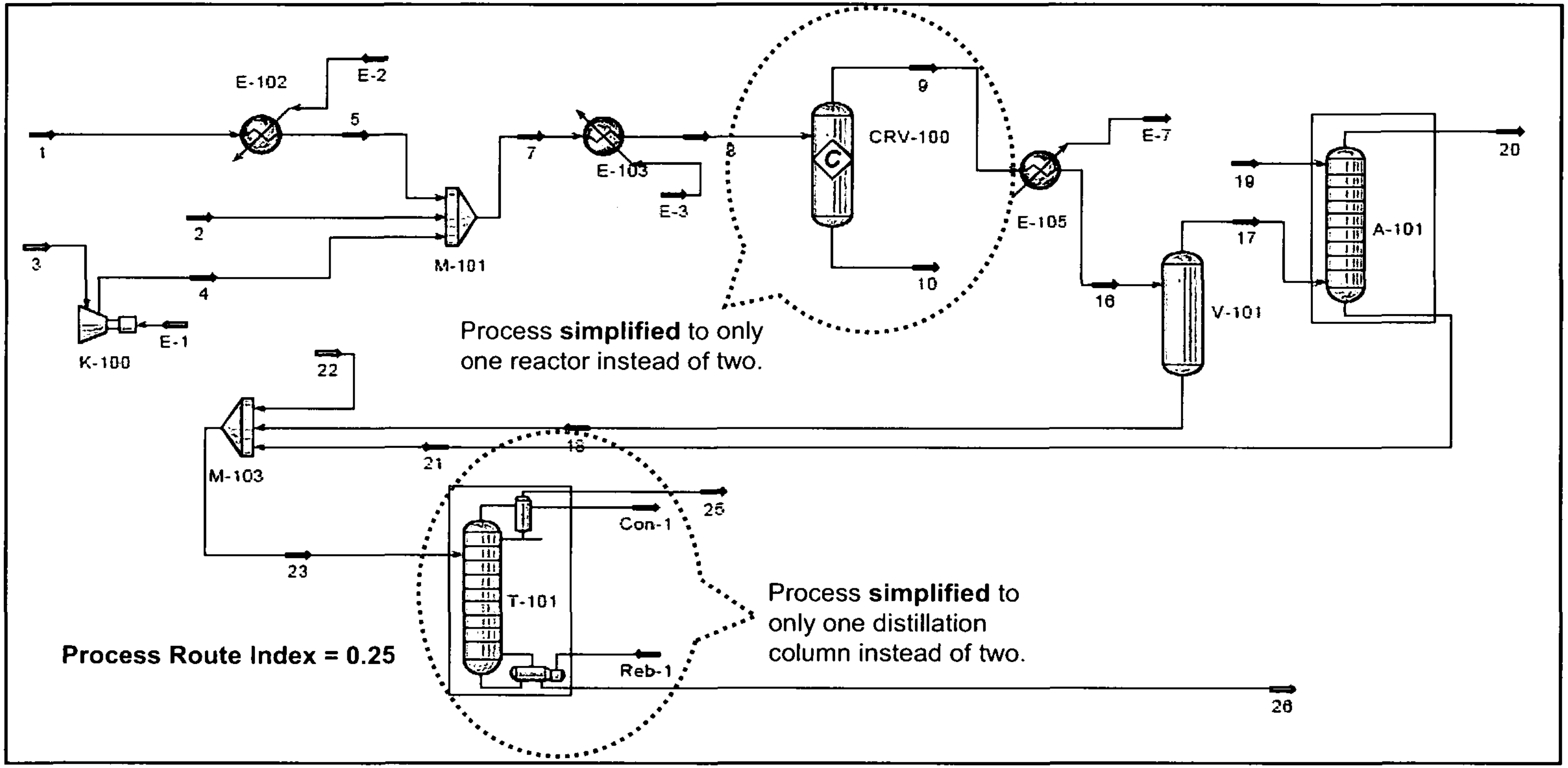


Figure 5.9 : Further simplified Acrylic Acid production simulation

5.5 Potential Damages Due to Explosion in Acrylic Acid Process

Apart from guiding inherent safety modification and producing the FN curve above, the ISIF is also capable to provide indication of various types of damages as a function of distance from the source of explosion. The calculation follows i-CET algorithm in Figure 4.6. The analysis is based on stream 18 of the simulation illustrated in Figure 5.9 and adopting similar assumption used in generating the FN curve above. The resulting overpressure as a function of distance from source of explosion is represented in Figure 5.10 which shows overpressure is maximum at a distance corresponding to approximately 50m from source of explosion and gradually reduces as distance increases.

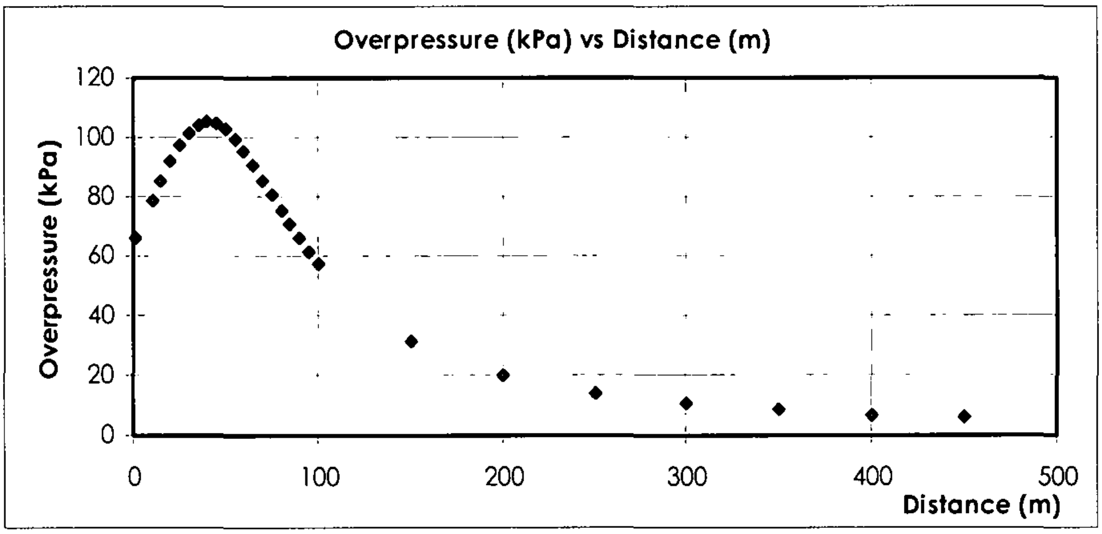


Figure 5.10 : Overpressure vs. Distance

The overpressure resulting from the explosion can cause damage of equipment and structures. The damages are estimated by using probit equation and relevant constants provided in Table 3.4. Figure 5.11 shows that an explosion due to leak in stream 18 can cause high probability of damage to structures up to approximately 100m from the source of explosion, following which the probability of such damage gradually reduce. Probability of damage to small equipment follows similar trend with the highest probability of 96% at approximately 50m from source of explosion.

Figure 5.12 is plotted to show the relationship between overpressure and probability of damage to equipment and damage to structure resulting from stream 18 of this simulation. It is important to note that this relationship is specific to this case only.

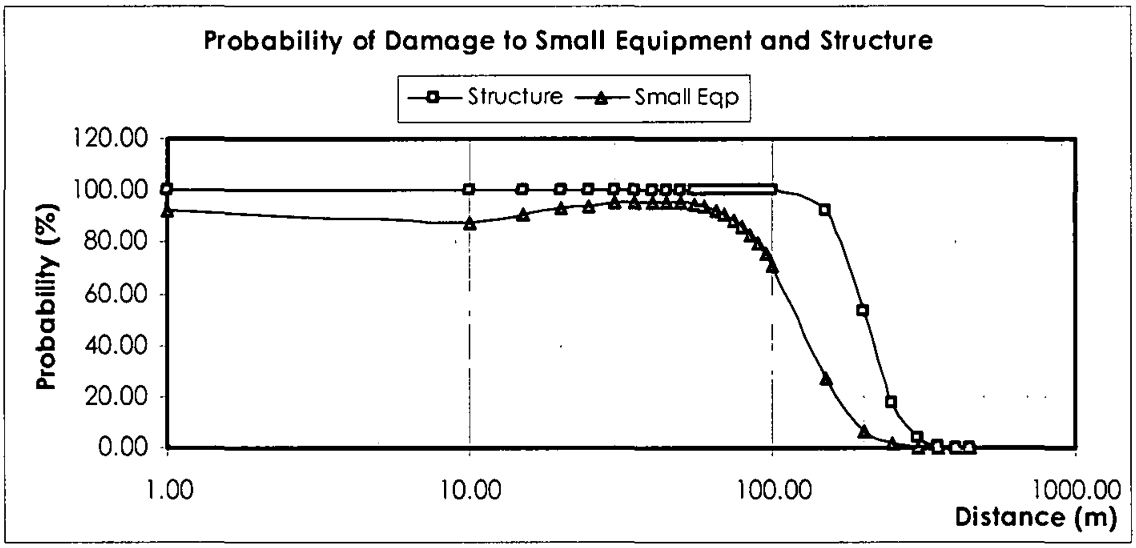


Figure 5.11 : Possible damages from explosion resulting from leak of stream 18 in Acrylic Acid simulation

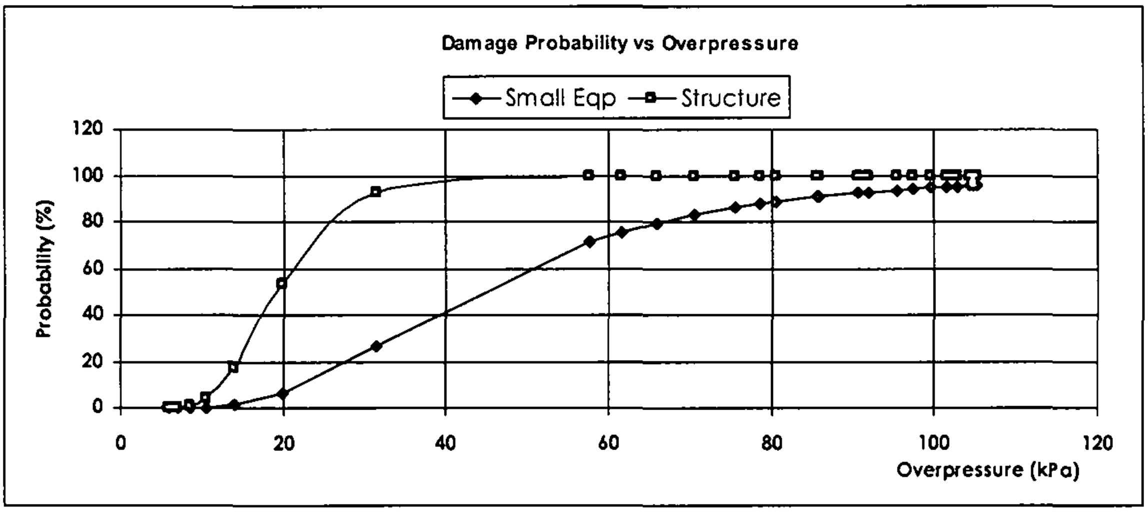


Figure 5.12 : Damage probability vs overpressure

Substituting different constants, C_i, for TNO correlation (Equation 3-19) the following distances are determined. Based on this table, location of control building should be located more than 145m from the potential source of explosion to avoid significant damage should such an incident occur.

Table 5.15 : Distances determined by TNO Correlation

Types of damages	Maximum distance (m) at which such damage can be expected based on TNO Correlation
Significant damage to building and process equipment	73
Repairable damage to building and damage to house facades	145

5.6 Attenuation of Process Pressure to Improve Inherent Safety Level

Figure 5.13 shows a distillation column, C2401, which separates the light ends and heavy ends of the hydrocarbon feed. The light-end products are produced at stream "To E-2405" while the heavy-end is produced in stream "To C-2501". The process feed is at high pressure i.e. 50bar. The main specification at the heavy-end is propane mole fraction. It should not exceed 0.20 to ensure minimal light component is entrained hence maximizing recovery of light components.

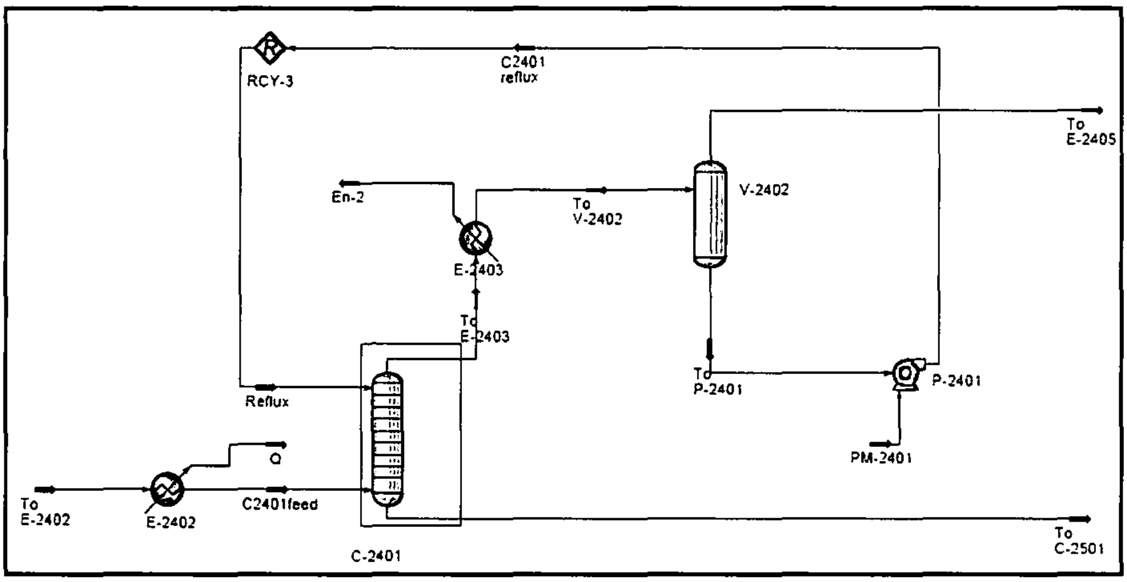


Figure 5.13 : Distillation Column

The Process Route Index for the base case is determined to be 5.66. The process stream having the highest Process Stream Index is "To C-2501" with a score of 18.69. Based on assumption that a leak developed and continued for 15 minutes in a 300mm pipe, the Inherent Risk due to "To C-2501" is determined and plotted in Figure 5.14. From this figure, it is determined that for the particular set of scenario, the resulting frequency of event and resulting death, is below the intolerable line established by the Malaysian authorities.

Adopting the ALARP philosophy as applied to safety, the present case study aims to lower the Inherent Risk of the process and at the same time meeting objective of the design i.e. to separate and recover light-ends.

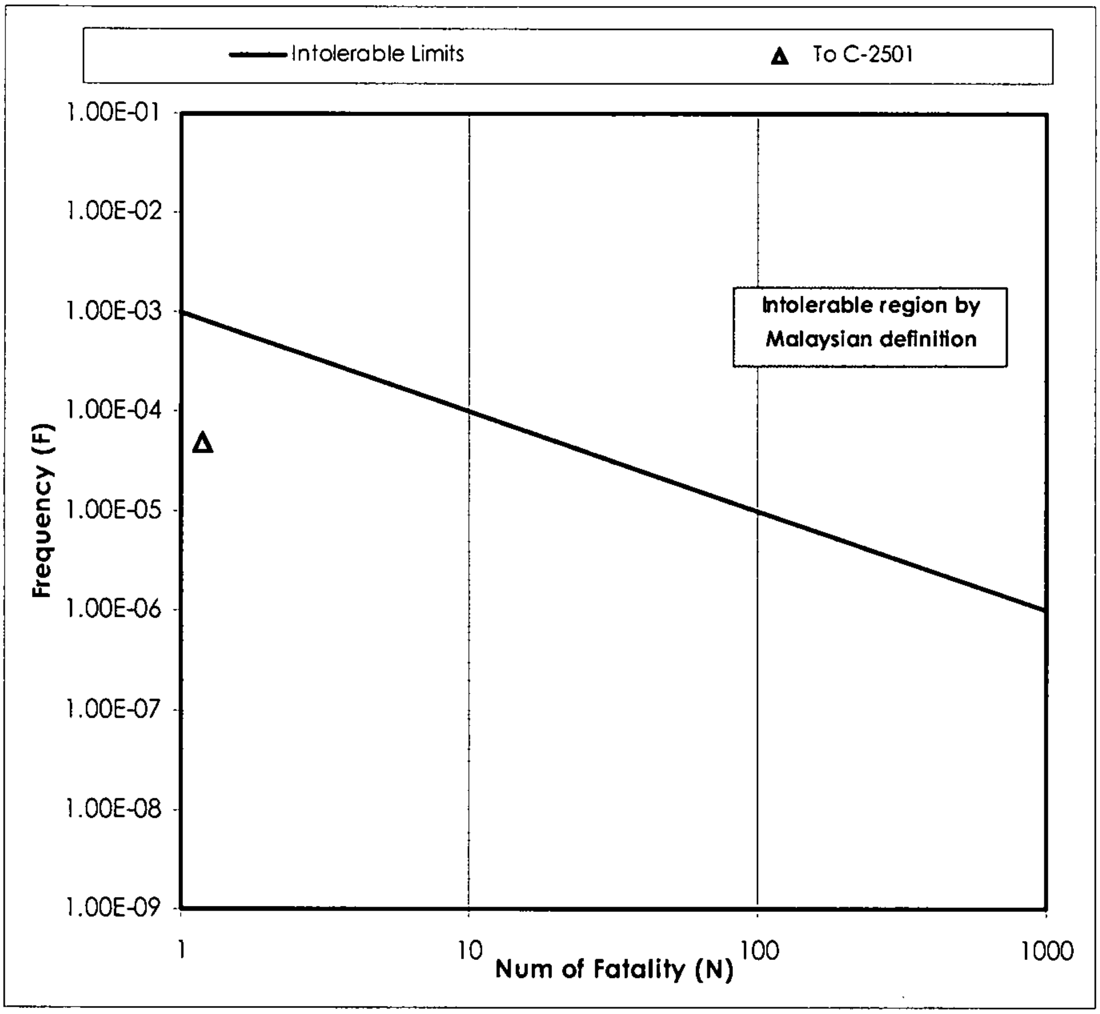


Figure 5.14 : FN curve for distillation column base case

Since the feed cannot be changed and there is no addition of process chemicals, the Inherent Safety principle of substitution cannot be applied. The process line up is a single distillation column with its accessories and hence does not present opportunity for simplification. There is an opportunity to apply the principle of attenuation to this case as the process pressure is approximately 50bar. Attenuation can be achieved by means of lowering the process pressure.

The distillation column pressure is reduced by steps of 5bars while checking product streams to ensure specifications are met. By reduction of pressure, the amount of hydrocarbon leaked to the environment in any incident will be lower, hence reducing the amount of risk inherent to this process. For every reduction of pressure, the PRI is recalculated and the results are tabulated in Table 5.16.

Table 5.16 : Distillation column pressure and PRI

Distillation Column Pressure	Process Route Index (PRI)
50	5.66
45	5.32
40	5.20
35	5.09
30	4.97
25	4.85
20	4.73

As expected, the PRI reduces as process pressure is attenuated to lower pressure. In the present case study, pressure can only be reduced to approximately 40bar in the distillation column. Figure 5.15 shows that for pressure lower than 40bar, mole fraction of propane in stream "To C2501" will increase above the 0.2 limit set above.

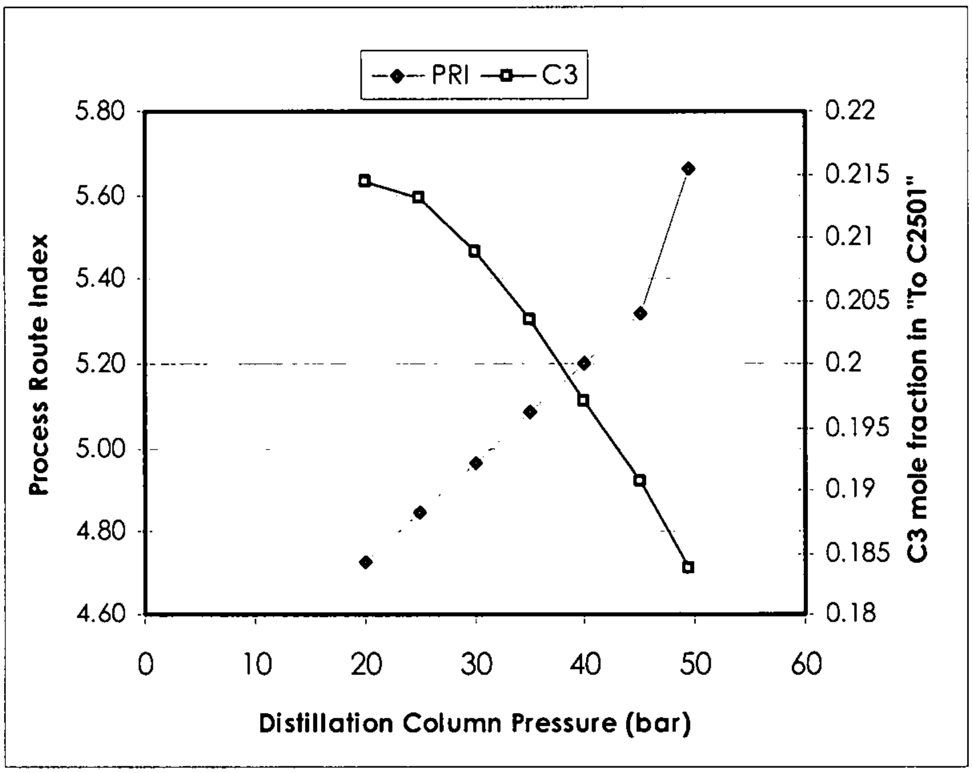


Figure 5.15 : PRI and C3 mole fraction vs. pressure

Based on the specification constrain and pressure attenuation to 40bar in this case study, the level of inherent safety improved by approximately 8.17% as determined by Equation 5-9. Future work is required to link this improvement to actual benefits for instance CAPEX or lifecycle cost. This case study clearly shows the application of

ISIF and the prototype developed in this research in enhancing inherent safety during process simulation.

5.7 Limitations of Inherent Safety Intervention Framework

The ISIF developed in this research has addressed a few challenges associated with applying inherent safety during process design. Mainly, ISIF is fully integrated with process simulation software, thus allowing concurrent assessment of inherent safety during process design and allowing for modifications to be carried out in the early stages. This has been demonstrated in the case studies above where ISIF can be used to guide the usage of Inherent Safety principles such as substitution, simplification and attenuation during process simulation and resulting in inherently safer processes. Secondly the enhanced inherent safety indices account for interaction of process parameters and composition of the process streams. This allows the PRI and PSI to represent the actual scenario more accurately compared to other indices developed prior to this work.

However, the ISIF still depends largely on experience of users to select the IS principles to be applied. Using PSI, the design engineer can determine the streams that can potentially cause larger damage however the decision of which IS principle is applicable in the particular situation is still a judgment call.

As with matters relating to safety, the level of inherent safety is highly subjective. At such, the proposed ISIF can only provide a measure of relativity in terms of level of inherent safety of a particular design compared to another. ISIF does not have a generic numerical limit than can be applied as a standard to determine acceptability of a particular design. At such, the present research uses a modified FN curve to represent potential frequency and fatality due a design under discussion. The modified FN curve would show if the design in intolerable or otherwise, based on Malaysian limits. In the present case studies, the limit of inherent safety modification is bounded by product specification or design intent of the plant under simulation.

CHAPTER 6

Conclusion and Future Works

6.0 CONCLUSION AND FUTURE WORKS

Application of Inherent Safety in the process industry is a very attractive proposition and is expected to bring benefits from safety and overall lifecycle cost perspectives. However its successful implementation has been hampered by non-availability of tools and systems which can be easily utilized by the industry. One of the major challenges is to be able to quantify different inherent safety levels (ISL) of various processes. Previous attempts to quantify ISL have limited application as there are several shortcomings as described in Section 2.7.

A few commonly used safety and hazard assessment tools deliberated in Section 2.1. Most of these techniques are often carried out in series and often towards the end of process design stages. The most comprehensive methodology is the Quantitative Risk Assessment (QRA). QRA is a very structured approach to quantify different sources of risk. The late identification and quantification of hazard led to very limited options to improve safety of the process.

The present research work proposes an integrated Inherent Safety Intervention Framework (ISIF) which combines the structured methodology of QRA with the ability to quantify ISL during preliminary design stages. The framework for ISIF integration into process design workflow is presented in Figure 4.1. ISIF has three main modules to quantify ISL, to estimate consequences and to estimate probability of an event. Each of the modules is described in detail in Section 4.1 and Section 4.2.

The two tier Inherent Safety Index (2t-ISI) has two levels of comparison i.e. the Process Route Index (PRI) and Process Stream Index (PSI). These two indices are based on interaction of few process parameters e.g. pressure, density, etc., unlike previous indices. The PRI is used to compare and rank different process routes while the PSI can be used to rank streams within a process to focus improvement efforts.

The PRI is validated against previous works in Chapter 5.0, which shows the present PRI agrees closely with expert opinion in ranking the level of inherent safety for MMA production but offers slightly different ranking when compared to acetic acid processes. The differences can be attributed to the different consideration that 2t-ISI take in developing the PRI. PSI on the other hand is validated against calculated explosion energy levels.

In order to represent risk level during initial design stage in a manner familiar to many, the present research proposed Inherent Risk Assessment (IRA), which is similar to QRA and results are presented using FN Curve. IRA can used to gauge initial acceptance of the process being designed as the inherent risk can be compared to the limits set by local authorities. Key comparisons of IRA and QRA are presented in Table 4.6.

In later parts of Chapter 5.0, the present research demonstrates the application of ISIF and its modules in illustrative examples to apply principles of Inherent Safety to improve inherent safety levels of a design. These examples clearly demonstrated that ISIF can be used as an integrated tool during process simulation to apply the principles of Inherent Safety such as substitution (selecting inherently safer feedstock), process conditions attenuation and process simplification. Apart from these, the research also shows the capability to quantify consequences of explosions. Having all these information generated during process simulation stage when changes can still be carried out relatively cost-free, the present research has produced a framework and the accompanying tools to enable application of Inherent Safety into designing inherently safer processes.

6.1 Recommendation For Future Works

In the course of conducting the research, a number of challenges are encountered. These challenges can be pragmatically seen as potential areas to be further researched and developed. A number of extension works based on the framework can also be pursued to further promote this concept and inherent safety in process design. These issues are summarized here to stimulate research interests.

The present work only presented consequence evaluation for vapor cloud explosion. In order to provide more comprehensive analysis, the present researcher proposes for complete development of consequence model for other hazards and to integrate them into the present i-CET.

The present framework is only capable of quantifying the inherent risks of a process. In order for the information to be fully maximized into benefit, an intelligent system should be developed to propose the most viable modification option. The system should be design to evaluate various design modification adopting IS principles and provide the optimum solution which considers safety as well as overall lifecycle cost.

Transient operations or conditions during process startup and shutdown phases can present hazard of greater magnitude due to its deviation from standard operating norms. At such, future works should develop models capable of representing risk and IS level during such operations.

APPENDICES

APPENDICES

Appendix A : Flammability Calculations For Mixture

Component	Mole Fraction	Lower Flammability Limit (LFL)	Upper Flammability Limit (UFL)
CO	0.41	12.5	74.2
Methanol	0.01	5.9	36
Acetic Acid	0.58	4	16

Equation 3-4 and Equation 3-5 are used to calculate the LFL and UFL for the mixture:

$$
\begin{aligned}
LFL_{mix} &= \frac{1}{\sum_{i=1}^{n} \frac{y_i}{LFL_i}} \\
&= \frac{1}{\frac{0.41}{12.5} + \frac{0.01}{5.9} + \frac{0.58}{4}} \\
&= \frac{1}{0.18} \\
&= 5.57
\end{aligned}
$$

$$
\begin{aligned}
UFL_{mix} &= \frac{1}{\sum_{i=1}^{n} \frac{y_i}{UFL_i}} \\
&= \frac{1}{\frac{0.41}{74.2} + \frac{0.01}{36} + \frac{0.58}{16}} \\
&= \frac{1}{0.04} \\
&= 23.78
\end{aligned}
$$

Appendix B : Base Failure Rates

Equipment	Type of leak	Frequency (failure per year)
Pipe Diameter = 25mm	Rupture leak	$1E^{-6}$ per meter
	Major leak	$1E^{-5}$ per meter
	Minor leak	$1E^{-4}$ per meter
Pipe Diameter = 100mm	Rupture leak	$3E^{-7}$ per meter
	Major leak	$6E^{-6}$ per meter
	Minor leak	$3E^{-5}$ per meter
Pipe Diameter = 300mm	Rupture leak	$1E^{-7}$ per meter
	Major leak	$3E^{-6}$ per meter
	Minor leak	$1E^{-5}$ per meter
Flanges	Section leak	$1E^{-4}$
	Minor leak	$1E^{-3}$
Valves	Rupture leak	$1E^{-5}$
	Major leak	$1E^{-4}$
	Minor leak	$1E^{-3}$
Pumps	Rupture leak	$3E^{-5}$
	Major leak	$3E^{-4}$
	Minor leak	$3E^{-3}$

Appendix C : Flammability Properties

(Source : Estimating The Flammable Mass of a Vapor Cloud, John L Woodward, 1999, CCPS AIChE, US)

High Explosives						
Materials	Flammability Limit (% v/v)		Stoichiometric in air	Auto Ignition Temperature	Min Ignition Energy in air	Net Heat of Combustion
	Lower	Upper	(% v/v)	(°K)	(mJ)	(MJ/kg)
Acetylene	2.4	80	7.72	578	0.017	48.22
Ethyl acetylene	2	11.5		699		40.02
Ethylene oxide	3	100	7.72	702	0.062	27.65
Hydrogen	4	72.5	29.5	673	0.011	119.95
1, 2 Propylene Oxide	2.1	21.5	4.97	722	0.13	30.74
1, 3 Propylene Oxide	2.8	37	4.97	722	0.14	31.01
Medium Explosives						
Materials	Flammability Limit (% v/v)		Stoichiometric in air	Auto Ignition Temperature	Min Ignition Energy in air	Net Heat of Combustion
	Lower	Upper	(% v/v)	(°K)	(mJ)	(MJ/kg)
Acetaldehyde	1.61	10.4	7.73	448	0.38	25.07
Acetone	2.5	11.6	4.97	810.9	1.15	28.57
Benzene	1.2	7.1	2.72	771	0.2	39.9
1-3 Butadiene	2	11.5	3.67	693	0.13	44.55
Butane	1.5	8.4	3.12	560	0.25	45.72
1-Butene	1.6	9.3	3.37	657	0.368	45.3
2-Butene-cis	1.6	9	3.37	598		45.17
2-Butene-trans	1.8	4.7	3.37	597		45.07
Carbon disulphide	1.2	44	6.53	363	0.009	14.5
Cyclohexane	1.1	7.8	2.27	518	0.22	43.44
Cyclopropane	2.4	10.4	4.45	771	0.17	46.56

n-Decane	0.6	4.7	1.33	474		44.2
Ethane	2.8	12.5	5.65	745	0.24	47.4
ethyl benzene	0.8	6.7	1.96	705		40.92
ethylene	2.7	36	6.53	723	0.07	47.12
ethyl mercaptan	2.8	18	4,45	568		27.93
n-Hexane	1.1	7.4	2.16	496	0.25	44.7
isobutane	1.8	8.4	3.12	733	0.25	45.58
2-isobutylene	1.8	8.8	3.37	738		44.98
isopentane	1.4	7.6	2.55	693	0.21	44.91
n-pentane	1.4	7.8	2,55	516	0.22	44.98
Propane	2	9.5	4.02	723	0.25	46.3
propylene	2	10.3	4.45	728	0.24	45.76
toluene	0.98	6.7	2.27	753	0.26	40.52
vinyl chloride	3.6	22	7.73	745		18.53
Low explosives						
Materials	Flammability Limit (% v/v)		Stoichiometric in air	Auto Ignition Temperature	Min Ignition Energy in air	Net Heat of Combustion
	Lower	Upper	(% v/v)	(°K)	(mJ)	(MJ/kg)
Ammonia	15	25	21.8	810	680	18.6
Ethanol	3.3	19	6.53	636	0.4	26.82
Methane	4.4	14	9.48	810	0.28	27.83
Methanol	5.9	36	12.25	658	0.14	19.8

Table A.0.1 : Tables Of Flammability Properties Of Common Chemicals (Woodward, 1999)

Appendix D : Sachs-Scale Distance Blast Curves Data Set

Blast = 10		Blast = 9		Blast = 8	
Scaled Distance	Sachs-Scaled Overpressure	Scaled Distance	Sachs-Scaled Overpressure	Scaled Distance	Sachs-Scaled Overpressure
0.253222	15.30934	0.2555624	4.977467	0.252876	2.008528
0.26886	13.41607	0.2770013	4.975857	0.301098	2.007472
0.277914	11.92243	0.3125786	4.973443	0.368274	2.006255
0.293086	10.30438	0.3342648	4.903614	0.421191	2.005444
0.307059	9.220397	0.3622681	4.767912	0.462668	1.963595
0.319529	8.137023	0.3873512	4.540755	0.501423	1.883107
0.334719	7.032894	0.4140737	4.062757	0.529015	1.793583
0.350649	6.163486	0.4279733	3.511663	0.565658	1.69644
0.369802	5.364079	0.4574386	3.034913	0.588803	1.593598
0.382315	4.969422	0.4824371	2.659665	0.625253	1.406324
0.392577	4.50913	0.5088284	2.363368	0.642119	1.29392
0.411314	4.091141	0.5294787	2.071263	0.672829	1.174031
0.425154	3.610539	0.5547504	1.879261	0.719251	1.01471
0.457451	3.056034	0.5850822	1.658363	0.753635	0.914328
0.479234	2.696885	0.6089066	1.504676	0.805316	0.799595
0.512216	2.314642	0.6336846	1.355796	0.84371	0.715481
0.529465	2.056948	0.6639128	1.221615	0.895858	0.635756
0.551068	1.905559	0.6909651	1.116117	0.957536	0.549445
0.57734	1.705102	0.7191198	1.019729	1.016773	0.49504
0.612992	1.494236	0.7534234	0.918808	1.086861	0.436827
0.637936	1.34639	0.7999701	0.8107848	1.154037	0.388153
0.66835	1.204755	0.8325447	0.7356462	1.23362	0.344892
0.700195	1.07057	0.8840027	0.6536747	1.336479	0.304319
0.753423	0.918808	0.9139153	0.6055813	1.447915	0.268519
0.805316	0.799595	0.9575361	0.5494449	1.600345	0.228837
0.84371	0.715481	1.003291	0.5054749	1.722227	0.203327
0.895858	0.635756	1.065303	0.4491509	1.878394	0.179403
0.957536	0.549445	1.116207	0.4132071	2.062468	0.157195
1.016773	0.49504	1.169544	0.3801397	2.310467	0.13489
1.086861	0.436827	1.267028	0.3331019	2.520105	0.12068
1.154037	0.388153	1.354402	0.295977	2.748765	0.107968
1.23362	0.344892	1.419159	0.274186	3.038618	0.095922
1.336479	0.304319	1.537488	0.2419307	3.336475	0.084633
1.447915	0.268519	1.665771	0.2164514	3.66372	0.075716
1.600345	0.228837	1.816724	0.1883522	4.023166	0.068209
1.722227	0.203327	2.008085	0.1627592	4.388091	0.060602
1.878394	0.179403	2.234553	0.14064	5.015995	0.052725
2.062468	0.157195	2.453592	0.1240883	5.544778	0.046519
2.310467	0.13489	2.730517	0.1094787	6.170429	0.040758
2.520105	0.12068	3.038618	0.09592168	6.959671	0.035958
2.748765	0.107968	3.381307	0.08288576	7.79714	0.031504
3.038618	0.095922	3.813503	0.0716176	8.50483	0.028381
3.336475	0.084633	4.358846	0.06102563	9.338992	0.025391
3.66372	0.075716	4.982435	0.05272646	10.25524	0.022874
4.023166	0.068209	5.695089	0.0452411	11.48987	0.020321
4.388091	0.060602	6.295627	0.04019347	12.78734	0.018179
5.015995	0.052725	7.053557	0.0357071	14.23059	0.016038
5.544778	0.046519	8.116755	0.03063707	16.15805	0.013954
6.170429	0.040758	9.093458	0.02684248	18.2243	0.012225
6.959671	0.035958	10.11979	0.02368216	20.55371	0.010563

7.79714	0.031504	11.48987	0.02032065	23.18146	0.009191
8.50483	0.028381	12.53337	0.01856226	26.14722	0.008165
9.338992	0.025391	13.57983	0.0168393	29.09985	0.007304
10.25524	0.022874	15.01258	0.01516946	32.82107	0.006399
11.48987	0.020321	16.48546	0.01366558	37.51656	0.005529
12.78734	0.018179	18.2243	0.01222538	41.75195	0.004912
14.23059	0.016038	19.61482	0.01124582	47.72511	0.004244
16.15805	0.013954	21.82922	0.009990834	54.18924	0.003692
18.2243	0.012225	24.29424	0.008937672	61.93688	0.003125
20.55371	0.010563	26.85744	0.008051383	69.85538	0.002719
23.18146	0.009191	29.89026	0.007202664	78.78834	0.002382
26.14722	0.008165	32.60234	0.00644393	87.68079	0.002101
29.09985	0.007304	36.28389	0.005764657	100.2325	0.001854
32.82107	0.006399	39.84161	0.005121623		
37.51656	0.005529	44.63816	0.004549949		
41.75195	0.004912	50.00954	0.003986408		
47.72511	0.004244	56.78308	0.00346834		
54.18924	0.003692	64.90326	0.002955387		
61.93688	0.003125	74.68624	0.002535754		
69.85538	0.002719	83.11789	0.002252775		
78.78834	0.002382	91.26781	0.002001483		
87.68079	0.002101	100.2273	0.001828242		
100.2325	0.001854				

Blast = 7		Blast = 6		Blast = 5	
Scaled Distance	Sachs-Scaled Overpressure	Scaled Distance	Sachs-Scaled Overpressure	Scaled Distance	Sachs-Scaled Overpressure
0.254091	1.017895	0.253579	0.498284	0.252925	0.199483
0.286726	1.017524	0.280444	0.498133	0.281604	0.199419
0.31498	1.017236	0.312243	0.497972	0.311437	0.199358
0.362666	1.016804	0.361936	0.497751	0.356188	0.199278
0.417572	1.016373	0.416731	0.497539	0.418455	0.199181
0.434734	1.01625	0.476592	0.490487	0.462786	0.199121
0.47435	0.995063	0.527072	0.48695	0.518732	0.199052
0.514103	0.967604	0.578965	0.473493	0.566013	0.196259
0.546046	0.921585	0.627485	0.460427	0.625878	0.18561
0.591796	0.88996	0.675494	0.441563	0.67829	0.176772
0.628554	0.841775	0.727178	0.423472	0.720449	0.169536
0.676632	0.801708	0.777547	0.400536	0.77548	0.155964
0.713852	0.758317	0.831455	0.386807	0.863158	0.140509
0.753104	0.712317	0.889047	0.365857	0.941648	0.129255
0.799866	0.669094	0.944269	0.346049	1.048113	0.116447
0.832578	0.624188	1.009715	0.331878	1.135772	0.107122
0.878342	0.582273	1.065257	0.313915	1.264209	0.097179
0.920403	0.539429	1.139044	0.296913	1.369942	0.089397
0.958063	0.506727	1.209794	0.280838	1.53504	0.079428
1.010724	0.472699	1.276341	0.265638	1.663424	0.073068
1.059124	0.437918	1.346523	0.249524	1.839142	0.066287
1.109821	0.402892	1.411059	0.234393	2.019858	0.060555
1.14757	0.386432	1.488649	0.220174	2.233186	0.054556
1.17864	0.368091	1.549529	0.205397	2.436211	0.049839

1.243376	0.338643	1.645776	0.194277	2.693564	0.045214
1.320452	0.307253	1.736271	0.182492	2.938386	0.04102
1.383657	0.282678	1.807278	0.170244	3.24885	0.037472
1.459654	0.260063	1.906692	0.16103	3.520569	0.034471
1.600345	0.228837	2.011495	0.150216	3.892546	0.03149
1.722227	0.203327	2.093799	0.14111	4.2181	0.028968
1.878394	0.179403	2.223852	0.13347	4.5101	0.027022
2.062468	0.157195	2.361936	0.125371	4.887303	0.024858
2.310467	0.13489	2.475139	0.117768	5.367428	0.022552
2.520105	0.12068	2.593768	0.110627	5.816335	0.020746
2.748765	0.107968	2.754822	0.103914	6.345238	0.019084
3.038618	0.095922	2.906357	0.09829	6.876059	0.017678
3.336475	0.084633	3.08682	0.092326	7.451286	0.016376
3.66372	0.075716	3.256553	0.086725	7.966948	0.01517
4.023166	0.068209	3.43562	0.081464	8.633435	0.014052
4.388091	0.060602	3.624532	0.076523	9.355494	0.012927
5.015995	0.052725	3.927595	0.069908	10.20603	0.011809
5.544778	0.046519	4.115756	0.065215	11.20888	0.010788
6.170429	0.040758	4.371228	0.060835	12.22815	0.009924
6.959671	0.035958	4.705217	0.056354	13.25086	0.009129
7.79714	0.031504	5.015995	0.052725	14.2633	0.008457
8.50483	0.028381	5.544778	0.046519	15.66513	0.00778
9.338992	0.025391	6.170429	0.040758	17.43626	0.007009
10.25524	0.022874	6.959671	0.035958	19.40764	0.006314
11.48987	0.020321	7.79714	0.031504	23.56534	0.005161
12.78734	0.018179	8.50483	0.028381	26.23071	0.004714
14.23059	0.016038	9.338992	0.025391	29.58988	0.004188
16.15805	0.013954	10.25524	0.022874	32.93408	0.003721
18.2243	0.012225	11.48987	0.020321	37.40121	0.003283
20.55371	0.010563	12.78734	0.018179	41.07548	0.002979
23.18146	0.009191	14.23059	0.016038	45.71956	0.002684
26.14722	0.008165	16.15805	0.013954	49.54235	0.002452
29.09985	0.007304	18.2243	0.012225	56.26221	0.002163
32.82107	0.006399	20.55371	0.010563	62.6221	0.001935
37.51656	0.005529	23.18146	0.009191	68.77404	0.001756
41.75195	0.004912	26.14722	0.008165	76.54977	0.001582
47.72511	0.004244	29.09985	0.007304	84.06995	0.001435
54.18924	0.003692	32.82107	0.006399	89.88798	0.001329
61.93688	0.003125	37.51656	0.005529	100.0568	0.001223
69.85538	0.002719	41.75195	0.004912		
78.78834	0.002382	47.72511	0.004244		
87.68079	0.002101	54.18924	0.003692		
100.2325	0.001854	61.93688	0.003125		
		69.85538	0.002719		
		78.78834	0.002382		
		87.68079	0.002101		
		100.2325	0.001854		

Blast = 4		Blast = 3		Blast = 2	
Scaled Distance	Sachs-Scaled Overpressure	Scaled Distance	Sachs-Scaled Overpressure	Scaled Distance	Sachs-Scaled Overpressure
0.254136	0.100397	0.251942	0.050181	0.251292	0.020089
0.281059	0.100366	0.280509	0.050165	0.279786	0.020083
0.312928	0.100334	0.310226	0.050149	0.31151	0.020076
0.355498	0.100295	0.357193	0.050128	0.363519	0.020067
0.417645	0.100247	0.416829	0.050105	0.412972	0.020059
0.517727	0.100182	0.464092	0.050089	0.466013	0.020052
0.580292	0.098768	0.516715	0.050072	0.515382	0.020046
0.624715	0.096044	0.56004	0.049371	0.566168	0.02004
0.668014	0.092111	0.598891	0.048344	0.634611	0.020033
0.723982	0.08895	0.623482	0.047673	0.687794	0.019481
0.789895	0.084713	0.666695	0.04572	0.745391	0.018553
0.822247	0.080689	0.717718	0.044152	0.791721	0.017794
0.915283	0.074738	0.777791	0.041471	0.852213	0.016483
0.959207	0.071682	0.842891	0.038952	0.929709	0.015163
1.018847	0.069226	0.895228	0.036588	1.0279	0.013661
1.09665	0.063244	0.950796	0.034131	1.121371	0.012566
1.19635	0.057776	1.044182	0.03075	1.248131	0.011243
1.322702	0.052052	1.17009	0.027895	1.361575	0.0102
1.442981	0.047883	1.267951	0.025661	1.495365	0.009318
1.606095	0.04284	1.411308	0.023119	1.631377	0.008631
1.752144	0.039409	1.539644	0.021267	1.815859	0.00783
1.937159	0.035259	1.713719	0.01916	1.967767	0.007253
2.08517	0.032662	1.857046	0.017625	2.190204	0.006489
2.336556	0.029425	2.039481	0.01599	2.373428	0.006011
2.515035	0.027069	2.239882	0.014607	2.641773	0.005416
2.81819	0.024218	2.509921	0.01316	2.862718	0.004982
3.074399	0.022124	2.719785	0.012022	3.165002	0.004457
3.353836	0.020072	3.02729	0.010831	3.476066	0.0041
3.708197	0.018336	3.280542	0.010033	3.84319	0.003694
4.045161	0.01652	3.651446	0.009039	4.164535	0.003375
4.413004	0.015197	4.01024	0.008257	4.604552	0.003083
4.944936	0.013596	4.433955	0.007543	5.023067	0.002797
5.358507	0.012507	4.804978	0.007036	5.590985	0.00252
6.004405	0.01119	5.348135	0.006295	6.05847	0.002302
6.506459	0.010223	5.834577	0.005831	6.788741	0.002059
7.097979	0.009339	6.494118	0.005217	7.307299	0.001895
7.795586	0.008591	7.03753	0.004866	8.0789	0.001695
8.676969	0.007739	7.938775	0.004323	8.932679	0.001559
9.277636	0.007219	8.488341	0.004033	9.876102	0.001405
10.18867	0.006459	9.511501	0.003608	10.70188	0.001283
11.34128	0.005942	10.307	0.003319	11.91163	0.001148
12.45544	0.00539	11.47233	0.00299	12.90786	0.001056
13.22883	0.005063	12.51555	0.002751	13.52704	0.001006
14.05107	0.004856	13.93059	0.002478		
15.43113	0.004375	15.19706	0.002264		
16.83435	0.004025	16.68968	0.00204		
18.24229	0.003702	18.32998	0.001876		
20.0344	0.003359	20.13031	0.00169		
22.44973	0.003026	22.10833	0.001544		
24.82125	0.002745	24.60745	0.001382		
27.62704	0.002456	26.84512	0.001271		

31.79655	0.002122	29.28453	0.001145
35.39152	0.001912	32.59678	0.001046
38.60983	0.001759	33.7055	0.001003
42.97345	0.001563		
47.8321	0.001408		
52.17964	0.001277		
57.6906	0.001151		
67.29609	0.001001		

Blast = 1	
Scaled Distance	Sachs-Scaled Overpressure
0.250801	0.010041
0.279239	0.010038
0.308821	0.010035
0.35797	0.01003
0.41494	0.010026
0.465102	0.010022
0.510933	0.01002
0.557525	0.010017
0.62073	0.009944
0.650582	0.009874
0.677282	0.00967
0.729101	0.009274
0.774449	0.009018
0.817065	0.00859
0.891329	0.007793
0.965895	0.007219
1.0823	0.006414
1.172864	0.005982
1.305471	0.00539
1.414654	0.004958
1.574598	0.004467
1.717782	0.004109
1.899206	0.003702
2.057966	0.003359
2.290733	0.003068
2.49899	0.002803
2.744543	0.00256
2.994057	0.002339
3.332441	0.002078
3.635474	0.001912
3.992542	0.001722
4.355515	0.001574
4.913486	0.001418
5.253418	0.001304
5.886651	0.001167
6.378857	0.001066
6.729741	0.001008

Appendix E : Heikkilä Inherent Safety Index

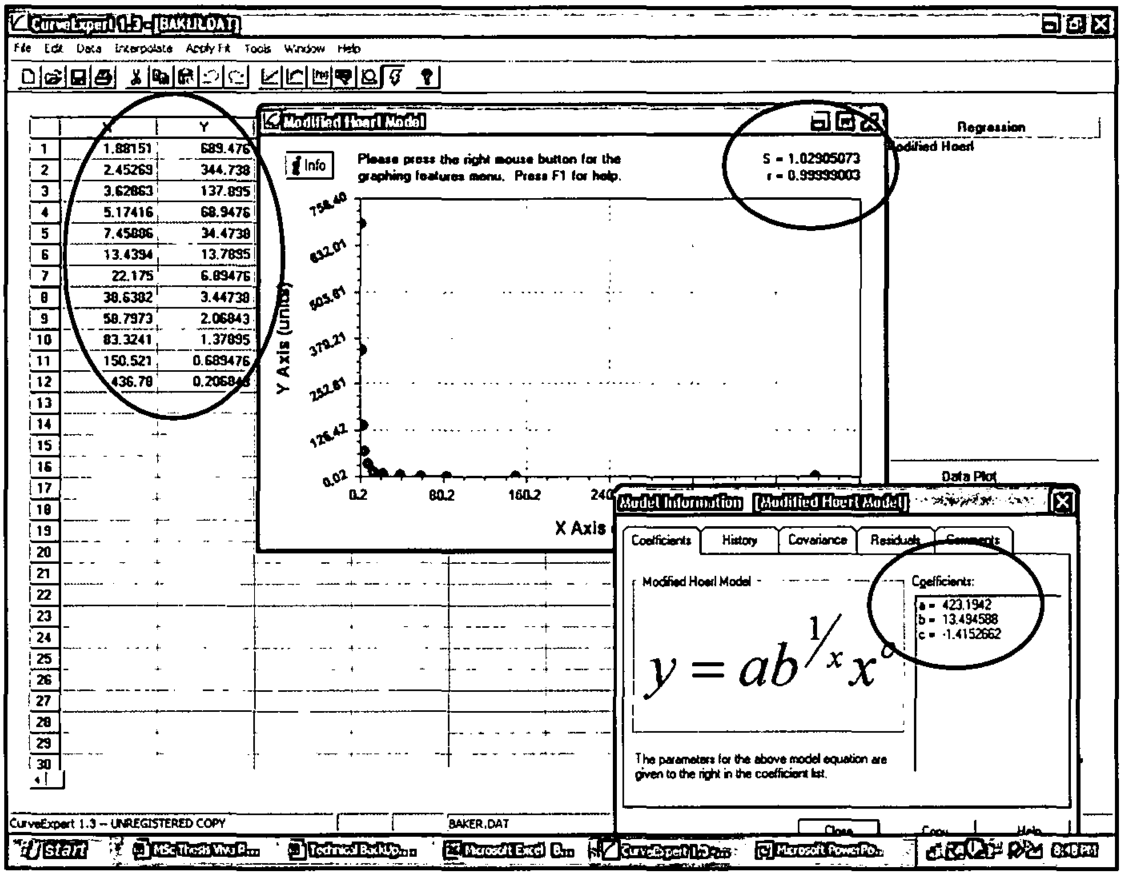
ISI by Hekkila (1999)	Basis	Parameters		Scale
Inventory	Scaled from Mond values by using expert recommendations in Lawrence's work. Different for ISBL and OSBL.	ISBL (tons)	OSBL (tons)	Score
		0 – 1	0 – 10	0
		1 – 10	10 – 100	1
		10 – 50	100 – 500	2
		50 – 200	500 – 2000	3
		200 – 500	2000 – 5000	4
		500 – 1000	5000 – 10000	5
Temperature	Base on the danger to posed to human, material strength. Beyond 300°C carbon steel strength is decreased considerably compared to room temperature.	<0 °C		1
		0 – 70 °C		0
		70 – 150 °C		1
		150 – 300 °C		2
		300 – 600 °C		3
		>600 °C		4
Pressure	Based on the DOW E&F Index	0.5 – 5 bar		0
		0 – 0.5 or 5 – 25 bar		1
		25 – 50 bar		2
		50 – 200 bar		3
		200 – 1000 bar		4
Heat of reaction	Heat released / absorbed by reaction can be calculated using standard enthalpy change formula. From safety point of view, it is important to know, how exothermic the reaction is. The classification used by King (1990)	≥3000J/g		4
		<3000J/g		3
		<1200 J/g		2
		<600J/g		1
		≤ 200J/g		0
Flammability	Classified based on EU directives	Non flammable		0
		Combustible (fp >55°C		1
		Flammable (fp < 55°C)		2
		Easily flammable (fp <21°C)		3
		Very flammable (fp <0°C and bp <35°C)		4
Explosiveness	Sub dividing the difference between UEL and LEL	Non explosive		0
		0 – 20		1
		20 – 45		2
		45 – 70		3
		70 – 100		4
Corrosiveness	Based on construction materials required	Carbon steel		0
		Stainless steel		1
		Better materials		2
Toxicity	Classified based on MOND index	TLV > 10000		0
		TLV ≤ 10000		1
		TLV ≤ 1000		2
		TLV ≤ 100		3
		TLV ≤ 10		4
		TLV ≤ 1		5
		TLV ≤ 0.1		6

Chemical interaction	Based on EPA's matrix (Hatayama et. al., 1980). Used to consider unwanted reactions of process substances with materials in the plant area. These reactions are not expected to take place in reactor and therefore not discussed in side reaction index.	Heat formation	1 to 3
		Fire	4
		Formation of harmless, nonflammable gas	1
		Formation of flammable gas	2 to 3
		Explosion	4
		Rapid polymerization	2 to 3
		Soluble toxic chemicals	1
		Formation of toxic gas	2 to 3

Type of equipment	Based on various studies and statistics of failures and qualitative arguments the following set of index is derived and used.	**ISBL Equipment type**	**Score**
		Equipment handling nonflammable, non toxic materials	0
		Heat exchanger, pumps, towers, drums	1
		Air coolers, reactors, high hazard pumps	2
		Compressors, high hazard reactors	3
		Furnaces, fired heaters	4
		OSBL Equipment type	**Score**
		Equipment handling nonflammable, non toxic materials	0
		Atmospheric tanks, pumps	1
		Cooling towers, compressors, blowdown systems, pressurized or refrigerated storage tanks	2
		Flares, boilers, furnaces	3

Safety of process structure	Based on experience and knowledge. Qualitative arguments	Recommended (based on standards)	0
		Sound engineering practice	1
		No data or neutral	2
		Probably unsafe	3
		Minor accidents	4
		Major accidents	5

Appendix F : Print Screen of Regression Software



	X	Y
1	1.88151	689.476
2	2.45263	344.738
3	3.62863	137.895
4	5.17416	68.9476
5	7.45886	34.4738
6	13.4394	13.7895
7	22.175	6.89476
8	38.6382	3.44738
9	58.7973	2.06843
10	83.3241	1.37895
11	150.521	0.689476
12	436.78	0.206843

Figure A.0.1 : Print screen of regression software tool

The print screen above shows the data from Baker for Overpressure and Scaled Distance are entered on the left side. The coefficients for the correlation are shown at the bottom right window while the standard error, s, and correlation coefficients are give in the top center window.

Appendix G : Explosion Effects and Damage Table (Clancey, 1972)

Overpressure (psi)	Damages observed
0.02	Annoying noise (137dB if of low frequency (10 to 15Hz)
0.03	Occasional breaking of large glass windows already under strain
0.04	Loud noise (143dB), sonic boom, glass failure
0.10	Breakage of small windows under strain
0.15	Typical pressure for glass breakage
0.30	"safe distance" probability 0.95 no serious damage beyond this value; projectile limit; some damage to house ceiling; 10% window broken
0.40	Limited minor structural damage
0.50	Large and small windows usually shattered; occasional damage to window frames
0.70	Minor damage to house structures. Large and small windows usually shattered; occasional damage to window frames
1.00	Partial demolition of houses, made uninhabitable. Large and small windows usually shattered; occasional damage to window frames
1 to 2	Corrugated asbestos shattered; corrugated steel or aluminum panels, fastenings fail, followed by buckling; wood panels (standard housing) fastening fail, panels blown in
1.30	Steel frame of clad building slightly distorted
2.00	Partial collapse of walls and roofs of houses
2 to 3	Concrete or cinder block walls, not reinforced, shattered. Destruction of cement walls 20 to 30cm width.
2.30	Lower limit of serious structural damage
2.50	50% destruction of brickwork of houses. Distortion of steel frame buildings.
3.00	Heavy machines (3000lb) in industrial building suffered little damage; steel frame building distorted and pulled away from foundations
3 to 4	Frameless, self-framing steel panel building demolished; rupture of oil storage tanks
4.00	Cladding of light industrial building ruptured
5.00	Wooden utility poles snapped; tall hydraulic press (40000lb) in building slightly damaged
5 to 7	Nearly complete destruction of houses
7.00	Loaded train wagon overturned
7 to 8	Brick panels, 8 to 12 inches thick, not reinforced, fail by shearing of flexure
9.00	Loaded train box cards completely demolished
10.00	Probable total destruction of buildings; heavy machines tools (7000lb) moved and badly damaged, very heavy machines tools (12000lb) survived
300.00	Limit of crater lip

Appendix H : Sample Calculation of Process Route Index

Parameters	Streams in HYSYS Simulation												
	CRV100t	CRV100b	E100out	V100top	V100bot	T100top	T100bot	O2 feed	ACH Rcy	ACH Feed	Offgas Rcy	K100out	P100out
Mass HV	11430.21	11430.21	11430.21	404.31	14690.74	18025.60	14553.38	0.00	18031.42	26936.03	404.48	404.48	18031.42
Density	3.27	0.89	54.03	10.22	1038.53	1042.37	862.77	12.70	1042.23	760.30	10.22	12.77	1042.19
ΔFL_{mix}	24.40	24.40	18.45	0.00	12.08	15.62	6.34	0.00	15.61	8.77	0.00	0.00	15.61
Pressure	10.00	10.00	10.00	8.00	9.00	5.00	5.00	10.00	5.00	10.00	8.00	10.00	10.00

$$\left.\begin{array}{r} \text{Average mass heating value} = 11195.19 \\ \text{Average stream density} = 490.97 \\ \text{Average } \Delta FL_{mix} = 9.74 \\ \text{Average pressure} = 8.33 \end{array}\right\} \quad \begin{array}{ll} \text{PRI} & = 11195.19 \times 49.97 \times 9.74 \times 8.33 \div 10^8 \\ & = 0.45 \end{array}$$

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